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Synthesis and Enzymatic Degradability of an Aliphatic/Aromatic Block Copolyester: Poly(butylene succinate)-*multi*-Poly(butylene terephthalate)

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Abstract: A novel multi-block copolyester, poly(butylene succinate)-*multi*-poly(butylene terephthalate) (m-PBST), was synthesized by the melt/solid interfacial co-polycondensation of a melt-blend of poly(butylene succinate) (PBS) and poly(butylene terephthalate) (PBT) that had been pre-formed. In this co-polycondensation, the reaction temperature was kept between the melting temperatures (T_m) of PBS and PBT so as for the low-melting PBS (melt) to be effectively connected with the high-melting PBT (solid). The succinate content and persistence ratio (r) of the resulting m-PBST were affected by the time of melt-blending of PBS and PBT where their chain-scrambling reaction was induced. The average block number per polymer chain became the largest (7.3) when the blending time was properly adjusted with a PBS to PBT ratio of 2:1. Owing to the block copolymer structure, m-PBST showed thermoplastic properties that should be intermediate between those of PBT and PBS and completely different from those of the corresponding PBS/PBT random copolymer. The enzymatic degradability of m-PBST was also confirmed by the use of Lipase PS® originated from *Pseudomonas cepacia*. Consequently, m-PBST ought to have potential applications as a new structural material with excellent soft/hard balance and toughness.

Keywords: poly(butylene succinate) (PBS), poly(butylene terephthalate), block copolymer, co-polycondensation.

Introduction

Currently, a large quantity of man-made plastics is utilized in daily life. These plastics, not existing in nature and non-biodegradable, likely cause serious waste problems after use and sometimes induce pollutions on the global environment when scattered in nature. One solution to these problems is to use bio-based or biodegradable plastics such as poly(*L*-lactide) (PLLA), poly(3-hydroxylalkanoate)s (PHA), poly(butylene succinate) (PBS), and their derivatives instead of the conventional petroleum-based non-degradable plastics.[1-7] These biodegradable polymers are readily assimilated into water and carbon dioxide in global environment, being environmentally benign. In addition, many of them can be derived from renewable natural resources, and their use is convinced to suppress the increase in atmospheric content of carbon dioxide even after their incineration. For example, PHA is directly bio-synthesized from glucose or edible oil by bacterial fermentation, being fully biobased. PLLA also retains the fully biobased nature because its starting L-lactic acid is a fermentation product although it is chemically polymerized by melt- and solid-state polycondensation of *L*-lactic acid or by ring-opening polymerization (ROP) of *L*-lactide, a cyclic dimer of *L*-lactic acid. On the other hand, PBS is chemically synthesized by combining both bio-originated succinic acid and oil-based 1,4-butanediol, being categorized as a partly biobased polymer. The synthesis of this aliphatic polymer is generally performed by the ordinary melt-polycondensation technique, while it has recently been shown that it can also be prepared by ROP of a cyclic dimer of butylene succinate.[8] At present, these biodegradable polymers are manufactured and utilized as packaging materials of foods and daily appliances as well as agricultural mulching films in a considerable scale. However, these biodegradable polymers have attained a limited size of market until now because of their poorer mechanical and thermal properties compared with those of the conventional oil-based polymers.[9-14] In particular, PBS polymers show very poor thermo-mechanical properties due to their low melting temperature (T_m=110 °C) in spite of showing very soft property due to the low glass transition temperature (T_g=-40 °C). The former unfavorable properties are mainly attributed to the weak cohesive energies of aliphatic esters, which can be increased by incorporating aromatic units into the main chain.[15-19] In fact, such introduction of aromatic units into aliphatic polyesters have been performed to obtain aromatic-aliphatic copolyesters such as poly(butylene adipate-*co*-terephthalate) (PBAT) and poly(ethylene adipate-*co*-terephthalate) (PEAT). The commercialized biodegradable

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*Corresponding Authors. E-mails: cwlee@hoseo.edu or ykimura@snr.kit.ac.jp polymers, Ecoflex® (PBAT), Easter-bio® (PBAT), and Biomax® (PEAT) manufactured by BASF, Eastman Chemical, and Du Pont, respectively, are those prepared by this approach and are ensured to have an improved thermal resistance together with modular biodegradability.[20] Since the ordinary copolyesters of PBAT are random copolymers of butylene adipate and butylene terephthalate (r-PBAT: poly(butylene adipate-*ran*-butylene terephthalate)), they ought to have an average or less than the average properties of the two component polyesters: poly(butylene adipate) (PBA) and poly(butylene terephthalate) (PBT).[15] Consequently, the above commercially available Ecoflex® and Easter-bio® are known to exhibit much lower T_m values than PBT and accordingly lower thermo-mechanical properties. In order to circumvent the properties of the aliphatic/aromatic copolyesters, the component units should be linked in blocky manner by which specific phase morphologies are formed to realize the relevant controlled properties reflecting the characteristics of the component polymer units.[21] It is, however, more difficult to synthesize such block copolyesters by the ordinary polycondensation technique because transesterification reaction between the two component polyesters likely produces random sequences. Therefore, so-called segmented polyesters have generally been prepared by chain extension of the corresponding oligomeric polyesters with coupling agents such as diisocyanates.[22-24] This technique, however, is not applicable for a large number of polymer combinations for which the reactivity and solubility of the prepolymers are crucially different. It has therefore been required to develop an efficient method to synthesize block copolyesters, particularly, those consisting of aliphatic and aromatic polyesters. Such aliphatic/aromatic block copolyesters ought to exhibit excellent properties in addition to characteristic biodegradation behavior. Previous studies on the biodegradability of r-PBST (Ecoflex® and Easter-bio®) revealed that the enzymatic degradability becomes lower with increasing the aromatic unit composition and that the degradability is lost when the aromatic unit ratio becomes higher.[25,26] However, no information is available on the enzymatic degradability of the related block copolyesters.

In this study a new technique is disclosed for directly synthesizing multi-block aliphatic/aromatic copolyesters by melt/solid interfacial co-polycondensation. Here we demonstrate the synthesis of poly(butylene succinate)-*multi*-poly(butylene terephthalate) (m-PBST) as a substitute of r-PBAT (Ecoflex® and Easter-bio®). This technique is to be an extension of the melt- and solid-state polycondensation of *L*-lactic acid that we developed for synthesizing high-molecular-weight PLLA directly from *L*-lactic acid.[27,28] In the step of this solid-state polycondensation, the oligomeric PLLA is allowed to crystallize to make its polymer tails and the catalysts concentrate in the amorphous domain for inducing the chain extension efficiently. In the present melt/solid interfacial co-polycondensation, the chain scrambling was first induced in a melt blend of high-molecular weight PBS and PBT to partially produce their block copolymers. Then, the polymer system was cooled to an appropriate temperature where the PBS and PBT segments kept melt and solid states, respectively, to conduct melt- and solid-state interfacial polycondensation. The inter-chain connection of the low-melting PBS segments with the high-melting PBT segments were successfully performed to obtain m-PBST. With the resultant m-PBST, the enzymatic degradability was examined using Lipase PS® from *Pseudomonas cepacia*[29,30] to compare it with that of its random counterpart, r-PBST.

Experimental

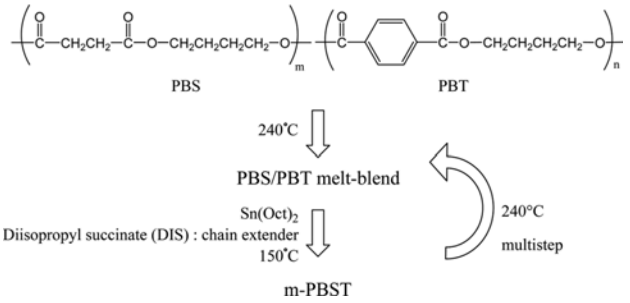
Materials. PBS and PBT were supplied by Mitsubishi Chemical Co., Ltd. (Yokkaichi, Japan). PBS had a weight-average molecular weight (M_w) of 51,200 Da with a dispersity in weight (M_w)/number (M_n) average molecular weight ratio of 2.1 and a T_m value of 111 °C. PBT had a M_w of 17,200 Da with M_w/M_n=2.0 and a T_m value of 219 °C. Both PBS and PBT were thoroughly dried in vacuum at 90 °C at least for 10 h before use.

Diisopropyl succinate (DIS) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and purified by distillation. Toluene and tin octoate ($S_n(Oct)_2$) were supplied by Nacalai Tesque Co. Ltd. (Kyoto, Japan) and purified by distillation before use. $Sn(Oct)_2$ was dissolved in a distilled toluene in a concentration of 0.1 g/mL. Lipase PS® was supplied by Amano Pharmaceutical Co., Ltd. (Nagoya, Japan). Its optimum pH and temperature were determined to be 6.0 and 50 °C, respectively, by using 1,2-*O*-dilauryl-*rac*-glycero-3-glutaric acid-resorufin ester as the substrate.[30,31] The catalytic activity of this lipase was 0.035 U/mg under the optimum conditions. Its k_{cat}/K_m was 23.7.

Measurements. The molecular weights were determined by gel permeation chromatography (GPC) using a Shimadzu analyzer system consisting of an LC-10ADvp pump, an RID-10A detector, and a C-R7A Chromatopac data processor. Samples were eluted out at 35 °C from a Shodex HFIP-806 column with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) containing sodium trifluoroacetate (1 mM) at a flow rate of 0.6 mL/min. The molecular weights were calibrated with poly(methyl methacrylate) (PMMA) standards, and the molecular weights of the samples were determined as the relative values.

500 MHz ^{1}H NMR spectra were measured on a Brucker ARX 500 spectrometer. For the measurement, the dichloromethane-insoluble products were dissolved in a *d*-trifluoroacetic acid/*d*-chloroform mixture (1/5 in volume ratio) in a concentration of 2-4 wt%, while the dichloromethane-soluble samples were dissolved in *d*-chloroform in 2-4 wt%. Tetramethylsilane (TMS) was used as the internal standard.

Differential scanning calorimetry (DSC) was carried out from -60 °C to 240 °C on a Shimadzu DSC-50 thermal analyzer under a nitrogen flow of 20 mL/min at a heating rate of 10 °C/min for about 1.7 mg of samples. T_m was taken as the peak temperature of the melting endotherm, and glass tran-



Scheme I. The melt/solid bi-phase polycondensation for synthesizing m-PBST.

sition temperature (T_g) was taken as the inflection point of the specific heat decrement at the glass transition.

Mechanical properties of polymer films were evaluated on a tensile testing machine (CATY-500BH: YONEKURA Ltd. Japan) at room temperature with a gauge length of 20 mm at a crosshead speed of 100 mm/min. The data obtained over five test specimens were averaged in each measurement.

Scanning electron micrographs (SEM) were observed with a Hitachi S-3000N microscope by accelerating the electron beam at an electric voltage of 5 kV. The samples for SEM were subjected to Au coating. The SEM observation was done with a Robinson detector at a sample tilting angle of 5°.

Synthesis of m-PBST. The multi block copolyester m-PBST was synthesized by the two procedures shown in Scheme I. The one is two-step procedure involving melt-blending of PBS and PBT and melt/solid biphase polycondensation in the 1st and 2nd stages, respectively. First, the thoroughly dried PBS and PBT were charged in a predetermined ratio and well mixed with a mechanical stirrer in melt state at 240 °C and 10 torr for a pre-fixed time. Then, a portion of the resulting melt-blend (4-5 g) was put into a steal separable mini-flask equipped with a mechanical stirrer and mixed with tin octoate (2.0 μmol/0.1 g of the melt-blend: 0.8 wt%) as the catalyst. In some cases, a certain amount of DIS was also added to it as a chain extender. The reaction system was heated at the conditions of 150 °C and 0.5-1.0 Torr with mechanical stirring for 24 h. Here, the PBT was well dispersed in the PBS melt with keeping the semi-crystalline or solid state. After the reaction, the product was extracted overnight with dichloromethane (CH_2Cl_2) being refluxed at 40 °C. The solution was separated by ultracentrifugation and evaporated to dryness, and the precipitate (CH_2Cl_2-insoluble part) was thoroughly dried in vacuum.

In the alternative multi-step procedure, the melt-blending and the melt/solid biphase polycondensation were repeated several times. As describe in the former procedure, both PBS and PBT were mixed well in a predetermined ratio in melt state at 240 °C and 10 Torr for 10 min. The melt-blend obtained was added with tin octoate (2.0 μmol/0.1 g of the blend) as the catalyst, and then the mixture was heated at the conditions of 150 °C and 0.5-1.0 Torr for 5 h. After this heating, the mixture was heated at 240 °C under stirring for 10 min in order to allow mixing of the two component polymers in melt state. The resulting melt-mixture was again subjected to the melt/solid polycondensation at the conditions mentioned above for 5 h. These high and low temperature processes were repeated twice further. The polymeric products were isolated as above.

The co-polycondensates thus obtained were identified as m-PBST; ^{1}H NMR ($CDCl_3$) δ=1.75 (m, C-CH_2CH_2-C of S$\underline{B}$S), 1.9 (m, C-CH_2CH_2-C of S$\underline{B}$T) 2.05 (m, C-CH_2CH_2-C of T$\underline{B}$T), 2.75(t, CO-CH_2CH$_2$-CO of S), 4.2 (m, C-CH_2-O of $\underline{B}$S), 4.5 (C-CH_2-O of $\underline{B}$T), 8.15 (m, -C_6H_4- of T) ppm. Here, S, B, and T denote the structural units of succinate, oxytetramethylenoxy, and terephthalate, respectively. The unit compositions of the repeating units BS (P_{BS}) and BT (P_{BT}) were calculated from the oxymethylene peaks of the BS (δ=4.2 ppm) and BT (δ=4.5 ppm) units, respectively. The persistence ratio (ρ) of the units was calculated by Eq. (1);[32]

$$\rho = 2\, P_{BS}P_{BT}/P_{SBT} \tag{1}$$

where P_{SBT} is the hetero diad ratio that can be calculated from the signal at d=1.9 ppm. The block lengths of PBS (L_{BS}) and PBT (L_{BT}) were determined by Eq. (2) and (3), respectively,

$$L_{BS} = 200\, P_{BS}/R = 2\, P_{BS}/P_{SBT} \tag{2}$$

$$L_{BT} = 200\, P_{BT}/R = 2\, P_{BT}/P_{SBT} \tag{3}$$

where R (=100 P_{SBT}) is the run number indicating the number of hetero ester bonds per 100 monomer units.

For comparison, r-PBST with a certain unit ratio was synthesized by the conventional melt-polycondensation of a mixture of dimethyl succinate, dimethyl terephthalate, and 1,4-butanediol at 230 °C.[30]

Polymer films of m-PBST, r-PBST, and PBT (0.1 mm thickness) were prepared by the ordinary melt-pressing technique at 230 °C. Polymer films of PBS were also prepared likewise at 130 °C.

Enzymatic Degradation. As previously reported,[30] one piece (4.0×0.5 cm in size) from each of the resultant films was immersed in a solution of Lipase PS® (5 mg/mL) in 0.1 M phosphate buffer (pH=6.0, 4.2 mL). After incubation at 50 °C for a pre-determined time, the film was removed from the solution, washed thoroughly with distilled water and with ethanol, and dried in vacuum for analysis. As a control experiment, the film was incubated in the 0.1 M phosphate buffer without the enzyme added at the same conditions and analyzed.

Results and Discussion

Formation of m-PBST by the Two-Step Procedure. In the two-step procedure, the commercially available PBS and PBT samples were first blended mechanically in melt state at 240 °C. The PBS to PBT blend ratio was set at 4/1 or 2/1 in weight, and the blending time was changed from 3 min to 20 min. Prolonged melt blending of PBS and PBT at 240 °C (above their T_m) caused their chain scrambling by transesterification reaction in excess to produce random copolyester r-PBST. Probably, this transesterification reaction ought to be induced by the catalysts that had been utilized for synthesizing PBT and PBS and remained in the polymer pellets supplied. On the other hand, the short-term melt-blending for 3-20 min in which the blending was insufficient gave a block copolymer species of PBS and PBT in partial. The resulting polymer blend involving the block copolymer species was then subjected to the following melt/solid interfacial polycondensation by heating it in vacuum at 150 ºC (between the T_m of PBS and PBT) where a melt (PBS)/solid (PBT) bi-phase reaction system was formed. In the polymerizations of the melt-blends prepared with short blending times (< 10 min), a small amount of DIS (30 μmol/0.1 g of the melt-blend) was added in order to promote the ester-interchange reaction in the melt/solid interface. The added amount of DIS was larger than 3 times that of the polymer end functionalities, which was estimated to be 8.3 μmol per 0.1 g of the melt-blend on the basis of its M_n. In the polymerizations of the melt-blends prepared with longer blending times (10-20 min), DIS was not added because of their well-mixing state achieved. Each of the melt-blends and melt/solid polycondensates thus obtained was extracted with CH_2Cl_2 to separate the unreacted PBS and PBS-rich copolymers from the block copolymers. Here, unreacted PBS and PBS-rich copolymers were removed by this extraction, whereas PBT-incorporating block copolymer remained as the insoluble part. Table I summarizes the results of the melt-blending and melt/solid polycondensation at different conditions. Here, the sample numbers B(x)y and P(x)y denote the melt-blends and melt/solid polycondensates obtained as the CH_2Cl_2-insoluble parts. The code number x (4 or 2) indicates the weight ratio of PBS relative to PBT at the melt-blending (corresponding to the PBS to PBT blend ratio 4/1 or 2/1 in weight), while y (3, 10, or 20) corresponds to the blending time (3, 10, or 20 min). Therefore, the melt/solid polycondensate P(x)y is prepared from the melt-blend B(x)y, both having the identical x and y values.

Figure 1 compares the typical ^{1}H NMR spectra of the CH_2Cl_2-insoluble parts of (a) the melt-blend and (b) the melt/solid

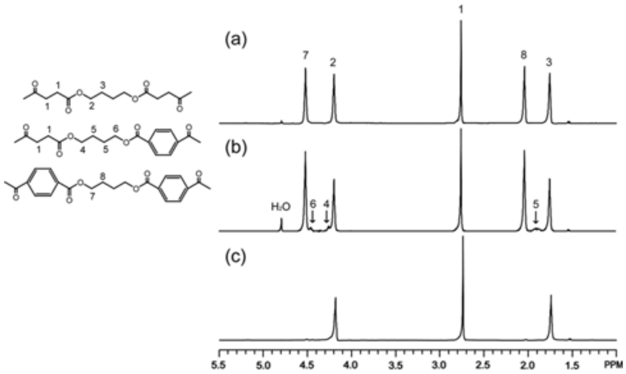


Figure 1. Typical ^{1}H NMR spectra of (a) the CH_2Cl_2-insoluble part of the melt-blend (B(4)20) and (b) the CH_2Cl_2-insoluble and (c) soluble parts of the melt/solid polycondensate (P(4)20).

Table I. Typical Results of Melt-Blending and Melt/Solid Polycondensation of PBS and PBT

	Reaction Step[a]	Time	C_2H_2-Insoluble Part						
Run No.	(PBS/PBT in feed: wt/wt)		Yield[a] (wt%)	M_w[b] (10^4 Da)	M_w/M_n[b]	P_{BS}/P_{BT}[c] (mol/mol)	L_{BS}[d]	L_{BT}[d]	ρ[e]
B(4)3	B (4.0/1.0)[f]	3 min	41	4.6	3.5	0.69/0.31	370	160	110
B(4)10		10 min	24	3.7	3.1	0.61/0.39	280	180	110
B(4)20		20 min	28	3.4	3.1	0.49/0.51	130	130	64
P(4)3	P (4.0/1.0)	24 h	26	2.3	2.3	0.41/0.59	14	20	8.1
P(4)10			26	4.2	3.0	0.39/0.61	11	17	6.5
P(4)20			24	2.1	2.1	0.20/0.80	4.6	19	3.7
B(2)3	B (2.0/1.0)[g]	3 min	38	2.4	2.2	0.30/0.70	23	53	23
B(2)10		10 min	35	2.2	2.2	0.28/0.72	14	36	14
B(2)20		20 min	30	2.0	2.0	0.13/0.87	4.1	29	4.1
P(2)3	P (2.0/1.0)	24 h	36	2.0	2.0	0.20/0.80	7.4	29	5.9
P(2)10			36	2.9	2.4	0.24/0.76	7.0	22	5.2
P(2)20			38	2.9	2.2	0.21/0.79	3.7	14	2.9
B(2)10m[h]	B(2.0/1.0)	10 min	35	2.1	2.1	0.28/0.72	37	96	27
P(2)10m[h]	P(2.0/1.0)	20.5 h[i]	30	3.2	2.3	0.42/0.58	8.8	12	5.1

[a] B: melt-blending at 240 °C. P: melt/solid co-polycondensation at 150 °C. The initial feed ratios of PBT were 20% and 33% in the B(4) and B(2) series, respectively. The polymer yield is for the CH_2Cl_2-insoluble part of the final product to be compared with the PBT ratio in the feed. [b] Determined by GPC. [c] Unit compositions of BS (P_{BS}) and BT (P_{BT}). [d] Block lengths of PBS (L_{BS}) and PBT (L_{BT}). [e] Persistence ratio. [f] Unit ratio: P_{BS}/P_{BT}=0.84/0.16. [g] Unit ratio: P_{BS}/P_{BT}=0.72/0.28. [h] Multi-step method involving 5 h melt/solid polycondensation for 4 times and 10 min melt-blending for 3 times. [i] Total reaction time.

polycondensate as compared with the spectrum of (c) the CH_2Cl_2-soluble part of the latter (Sample no. B(4)20 and P(4)20). Both spectra (a) and (b) exhibit the large signals due to the homo sequences of PBS and PBT, while spectrum (c) mostly shows the PBS signals, indicating that the CH_2Cl_2-soluble part of the melt/solid polycondensate consists preferentially of PBS homopolymer. The detection of PBS signals in the CH_2Cl_2-insoluble parts strongly support the fact that the PBS segments have formed block linkages with PBT segments. The small signals (No. 4-6) shown in spectrum (b) can be attributed to the hetero diads SBT, supporting the block copolymer structure of the CH_2Cl_2-insoluble parts. The same signals due to the hetero diads are also detected by magnification of spectrum (a) for the melt-blend in spite of their weak intensity. It is therefore evident that the chain scrambling has slightly been induced between the two polymers even in the melt-blending stage to form a partially block coploymer.

As noted in Table I, the yields of the CH_2Cl_2-insoluble products (PBT or PBT-rich part) became much larger than the initial feed ratios of PBT after the melt blending for a short blending time (B(4)3 and B(2)3), while they became lower after the melt blending for longer blending times (B(2)20. These results indicated that a considerable amount of PBS segments was incorporated into PBT by transesterification in the early stage of melt blending and that with increasing the blending time some of the introduced PBS segments as well as a small amount PBT units were eliminated into the PBS domain (CH_2Cl_2-soluble part) by the unit scrambling. Accordingly, the unit composition P_{BS} became higher in the melt-blends prepared with a short blending time and became lower with increasing the blending time until becoming almost 1/1 and 1/6.7 in B(4)20 and B(2)20, respectively. The block lengths L_{BS} and L_{BT} also grew shorter with increasing the blending time. On the other hands, the M_w values of the melt-blends decreased with the blending time, because of the loss of PBS segments together with some PBT units from the PBT-rich domain. In the case of B(2), the contents of the PBT or PBT-rich parts (CH_2Cl_2-insoluble) became only slightly higher or even lower (B(2)20) than the feed ratio of PBT (33 wt%), and the M_w values of this PBT-rich domains were comparable to that of PBT (1.72 kDa). From these results it is concluded that the melt-blends have already attained a nature of block copolymer, although they should consist of one or two long blocks and contain a considerable amount of the PBT homopolymers. Since the chain scrambling of PBS and PBT can be induced by the ester-interchange mechanism, further continuation of the melt-blending would lead to the formation of a random copolymer r-PBST.

After the melt/solid polycondensation, in return, the unit composition P_{BS} became lower in each CH_2Cl_2-insoluble part compared with the corresponding melt-blend, except the P(2)20 where the P_{BS} of the starting B(2)20 had been small. The P_{BS} of P(4)10 was almost twice that of P(4)20 and P(2)20, and the same unit composition of P(2)3, P(2)10, and P(2)20 were comparable with each other. Considering that the fully reacted P(2)20 and P(4)20 showed a similar P_{BS}, the P_{BS} of the melt/solid polycondensates ought to have preferentially been determined by the polymer compatibility of PBS and PBT. With these changes in P_{BS} and P_{BT}, the block lengths (L_{BS} and L_{BT}) became shorter and the persistence ratio (ρ) became lower. We think that the PBS segments that cannot accommodate in the solid PBT domain are likely to migrate from the block copolymer with further chain scrambling occurring between PBS and PBT. The M_w values of the CH_2CH_2-insoluble products became significantly higher than that of PBT. They changed with how much PBS segments had been introduced into or eliminated from the solid domain (CH_2Cl_2-insoluble part) during the melt/solid polycondensation. In the P(2) series having an almost similar content of PBS (P_{BS}), the molecular weights were comparable with each other although the block lengths of PBS and PBT were different from each other. In contrast, the sample P(2)10m, which was prepared by the multi-step method where the PBS/PBT reaction system was fused several times during the melt/solid interfacial polycondensation to enhance the hetero-chain scrambling, attained a higher P_{BS} and M_w values (vide infra).

Figure 2 shows the GPC curves of the CH_2Cl_2-insoluble parts of the representative melt-blends and the melt/solid polycondensates as compared with those of the starting PBS

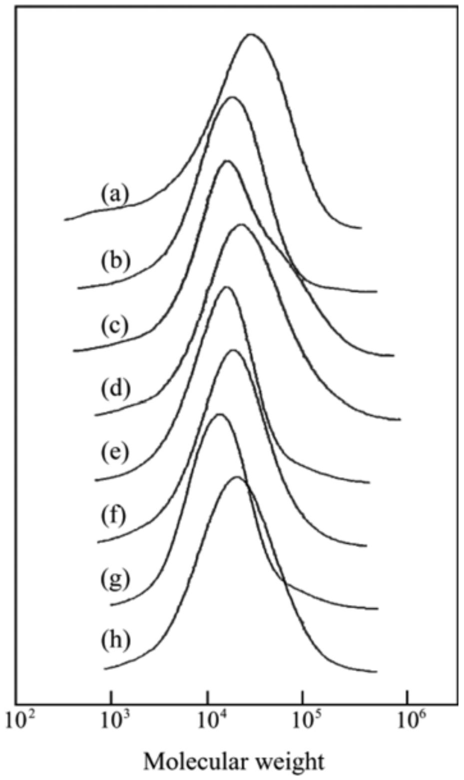


Figure 2. GPC curves of the starting (a) PBS and (b) PBT, the CH_2Cl_2-insoluble parts of the melt-blends (c) B(4)10, (e) B(2)10, and (g) B(2)10m and the melt/solid polycondensates (d) P(4)10, (f) P(2)10, and (h) P(2)10m.

and PBT. While the melt blend B(4)10 shows a shoulder peak at high molecular weight region probably due to the insufficient mixing of the two polymers, the other samples show their own single-modal curves. It is known that the curves of the melt/solid polycondensates shift to slightly larger molecular weight regions compared with those of the corresponding melt-blends. These data also support the formation of block copolyester of m-PBST.

The average numbers of the blocks involved in a copolymer chain can be calculated from L_{BS}, L_{BT}, and M_n. The resultant values are 3.0, 5.0, and 4.1 for P(4)3, P(4)10, and P(4)20, respectively, and 2.7, 3.9, and 7.3 for P(2)3, P(2)10, and P(2)20, respectively. These values support the multi-block structure of the CH_2Cl_2-insoluble polycondensates (m-PBST), having the least amount of PBT homopolymer, and the block length of m-PBST is strongly affected by the initial structure of the melt-blends that have exposed to the primary chain scrambling.

Figure 3 shows the DSC diagrams of the representative melt-blends and their melt/solid polycondensates. They show two endothermic peaks at the melting zones of PBS (T_{m1}) and PBT (T_{m2}) together with the glass transition behaviors of both blocks PBS (T_{g1}) and PBT (T_{g2}). Table II summarizes these values determined for various products. The detection of two broader melting endotherms for P(4)20 (T_{m1}) and for P(2)10 and P(2)20 (T_{m2}) is attributed to the formation of incomplete crystals. It is noted here that both T_{g1} and T_{g2} of the polycondensates are lower than those of the corresponding melt-blends. This may be attributed to the increased hetero diad units in the non-crystalline block sequences of the melt/solid polycondensates. These results show that PBS and PBT are immiscible in both crystalline and amorphous phases and that m-PBST should have a phase-separated structure.

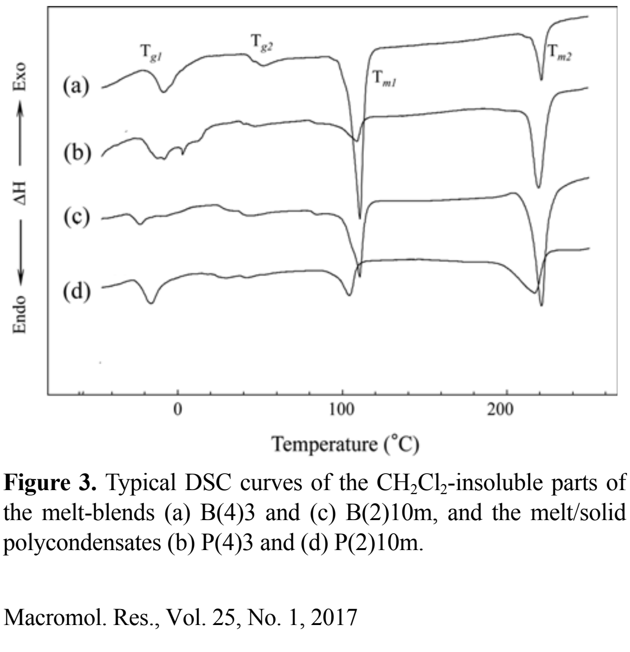


Figure 3. Typical DSC curves of the CH_2Cl_2-insoluble parts of the melt-blends (a) B(4)3 and (c) B(2)10m, and the melt/solid polycondensates (b) P(4)3 and (d) P(2)10m.

Formation of m-PBST by the Multi-Step co-Polycondensation. Figure 4 shows the time-dependent changes in M_w and P_{BS} in the multi-step melt/solid polycondensation where

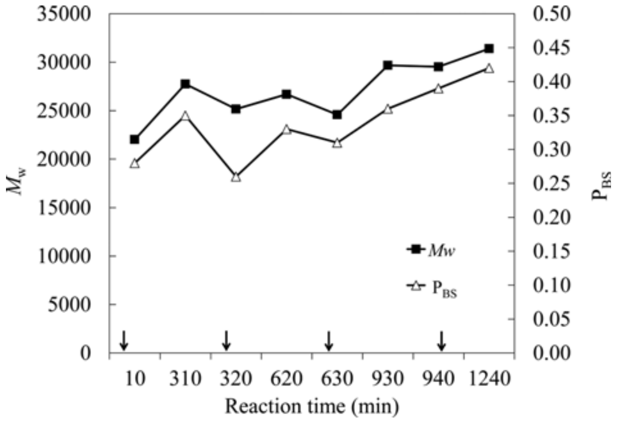


Figure 4. Changes in the unit composition (P_{BS}) and the weight-average molecular weight (M_w) with the total reaction time in the multi-step polycondensation (CH_2Cl_2-insoluble parts). The arrows ↓ indicate the points of conducting the melt-blending.

the melt-blending and melt/solid polycondensation were repeated several times. The melt-blending was done at 240 ºC for 10 min, and the melt/solid polycondensation was continued for 5 h at 150 ºC. As noted in Figure 4, the M_w of the product increases steadily with increasing the repeated number of melt/solid polycondensations although it significantly drops at each of the melt-blending steps. Figure 2(g) and 2(h) show the GPC curves of the initial melt-blend (B(2)10m) and the final polycondensation product (P(2)10m), respectively. A large molecular weight increase with single-modal curvature is noted after the multi-step polycondensation. The change in unit composition P_{BS} is similar to the M_w change in the repeated melt/solid polycondensation. It increases from 0.28 to 0.42 after 20 h in total time of melt/solid polycondensation. Figure 5 shows the changes in average block lengths (L_{BS} and L_{BT}) and the persistence ratio (ρ) as a function of total reaction time. Both L_{BS} and L_{BT} quickly decrease in the initial stage as does ρ. In the following stage, L_{BT} decreases steadily, while

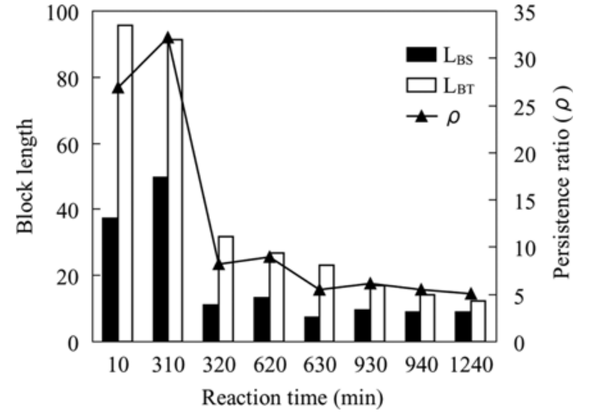


Figure 5. Average block lengths of PBT (L_{BT}) and PBS (L_{BS}) and persistence ratio (ρ) with the total reaction time in the multi-step polycondensation (CH_2Cl_2-insoluble parts).

Table II. Thermal Data of the C_2H_2-Insoluble Parts of the Melt-Blends and Melt/Solid Polycondensates (measured by DSC)

Sample	T_{g1} (°C)[a]	T_{g2} (°C)[a]	T_{m1} (°C)[b]	T_{m2} (°C)[b]
B(4)3	-18.1	41.2	110.9	221.5
B(4)10	-15.9	15.9	110.7	222.0
B(4)20	-21.1	8.5	110.9	221.1
P(4)3	-23.1	36.8	108.9	219.8
P(4)10	-14.7	32.1	109.0	214.3
P(4)20	-17.1	31.1	103.8, 110.1	216.0
B(2)3	-19. 5	14.7	107.0	221.6
B(2)10	-19.7	12.1	111.1	221.7
B(2)20	-14.1	10.9	108.6	220.0
P(2)3	-17.3	11.6	111.3	220.5
P(2)10	-22.4	12.9	110.8	210.7, 218.7
P(2)20	-19.4	11.7	107.9	207.9, 215.9
B(2)10m	-29.6	23.0	110.6	221.0
P(2)10m	-26.0	21.2	104.3	217.2

[a]Glass transition temperatures of PBS (T_{g1}) and PBT (T_{g2}) blocks. [b]Melting temperatures of PBS (T_{m1}) and PBT (T_{m2}) blocks.

L_{BS} remains almost constant. The characteristics of the initial melt-blend (B(2)10m) and the final product (P(2)10m) are summarized in the bottom rows of Tables I and II. The product P(2)10m is characterized by the large P_{BS} as compared with P(2)10 prepared from a similar initial melt-blend by the two-step method. The DSC diagram of P(2)10m (Figure 3(d)) also supports the phase separation structure of the both blocks in spite of the rather broader curvatures. This may be attributed to the relatively shorter average block lengths. The average number of blocks is estimated to be 6.8 for P(2)10m.

Mechanical Properties of m-PBST Films. Table III summarizes the mechanical properties of the polymer films of m-PBST and r-PBST as compared with those of the control films of PBS, PBT, and a PBS/PBT melt-blend, for which the polymer molecular weights are similar to each other. The m-PBST sample was prepared by the above multi-step melt/solid polycondensation while the r-PBST (a random copolymer) sample was synthesized by the ordinary melt-polycondensation of their monomers.[30] It is known that the m-PBST film has higher modulus and strength than the r-PBST film while having a much lower elongation. Compared with the PBS/PBT blend film, the m-PBST film is superior in tensile strength and elongation, having a similar modulus. It is therefore revealed that m-PBST resembles PBS and PBT in terms of strength and elongation, respectively, and has medium modulus of these two polymers. The comparable elongation at bleak of m-PBST with PBT may be due to the crystallization of the PBS segments involved in the former, which is in contrast with the case of r-PBST or the related PBAT (Ecoflex®) having a lower crystallinity at an identical unit composition.[30]

Degradability of m-PBST. Hydrolysis test of the polymer films was performed in the presence and absence of Lipase PS® originated from *Pseudomonas cepacia*. Figure 6 shows typical time courses of weight loss for the m-PBST films of P(2)20 prepared by the two-step process and P(2)10m prepared by the multi-step process, as well as for the film of r-PBST and the control film of PBS. The values in the parentheses

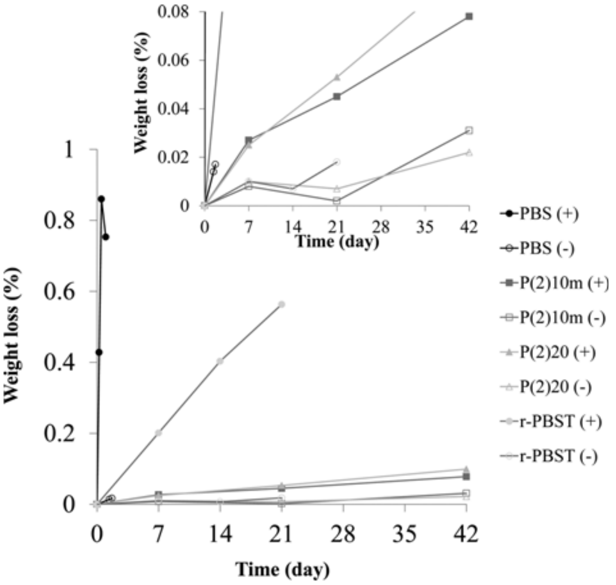


Figure 6. Weight losses as a function of incubation time for the m-PBST films as compared with those of PBS and r-PBST films; the closed and filled marks are for those incubated in the phosphate buffer (pH=6.0, control: (-)) and a buffer containing Lipase PS® (+), respectively.

Table III. Comparison of the Tensile Properties of Various Polymer Films

Polymer	P_{BS}/P_{BT}(mol/mol)	M_w (10^4 Da)	M_w/M_n	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
PBS	100/0	15.4	3.2	130	27	350
PBT	0/100	2.4	2.2	1,400	62	10
PBS/PBT[a]	43/57	2.9	3.0	590	6.8	2.3
r-PBST	38/62	2.2	2.0	180	19	370
P(2)10m	42/58	2.0	2.1	660	28	10

[a]Melt-blend.

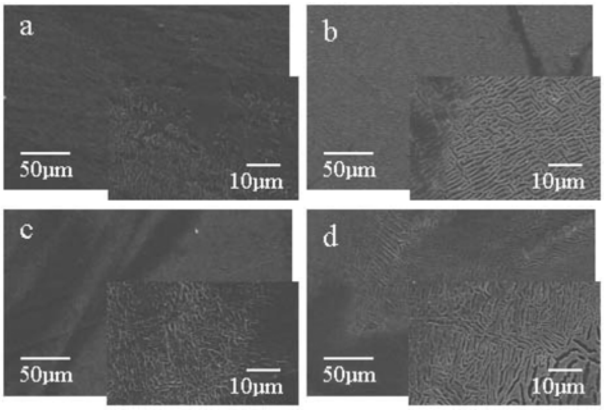


Figure 7. Typical SEM micrograms of the r-PBST films incubated in the (a) absence and (b) presence of Lipase PS® and the P(2)10m films incubated in the (c) absence and (d) presence of Lipase PS®. The incubation time was 6 weeks.

indicate the BS to BT unit ratios in %. When incubated in the phosphate buffer (control) without the enzyme added (-), intrinsically no weight loss is shown in each film. By the action of the lipase (+), the PBS film is quickly hydrolyzed to exhibit a sharp weight loss, while the films of P(2)10m, P(2)20 and r-PBST having higher P_{BT} are very slowly hydrolyzed. It is therefore revealed that the hydrolysis rate of both m- and r-PBST with Lipase PS® increases with increasing P_{BS}. This tendency is identical with the previously reported data that the biodegradability of r-PBST becomes lower with increasing the aromatic unit composition P_{BT}.[25,26] At the higher P_{BT}, in return, m-PBST shows higher degradability than r-PBST, because the PBS domain is formed in much larger size in the former block copolymer films than in the latter random copolymer films. In the commercially available random copolyester PBAT (*e.g.*, Ecoflex®), the enzymatic degradability ought to be similar to that of r-PBST.[30]

Figure 7 shows the SEM photos of the films of r-PBST and P(2)10m incubated in the presence and absence of Lipase PS®. The r-PBST film incubated in the absence of the enzyme (Figure 7(a)) shows few degradation sites with the crystal domain randomly distributed in the surface. In the same film enzymatically degraded (Figure 7(b)), in return, a lamella structure is clearly shown probably because of the surface crystallization of the residual polymers having survived the hydrolysis. The m-PBST film incubated in the absence of the enzyme (Figure 7(c)) shows little morphological change in comparison with its original film (data not shown), although a lamella structure has been created because of the phase separation behavior of the long blocky sequences. After the enzymatic hydrolysis (Figure 7(d)), the lamella structure becomes much clearer because the amorphous PBS-rich phase has been removed. The lamella size is larger in the m-PBST film than in the r-PBST film, both enzymatically degraded, and the cracks formed by the degradation are also larger in the former.

Conclusions

The multi-block copolyester m-PBST was successfully synthesized by the melt/solid interfacial co-polycondensation of the melt-blend of PBS and PBT. In this polymerization system, the low-melting PBS could be connected with the high-melting PBT at reaction temperature lower than T_m of PBT and higher than T_m of PBS. The P_{BS} and r of the resulting m-PBST became lower with the blending time used for making the melt-blend of PBS and PBT. The average number of blocks comprised in one macromolecular chain of m-PBST was the largest (7.3) when synthesized from the melt-blend that had been prepared with a blending time of 20 min at PBS/PBT=2/1. m-PBST was found to be degraded by the enzymatic hydrolysis in the presence of Lipase PS® from *Pseudomonas cepacia*. The enzymatic hydrolyzability of m-PBST was different from that of r-PBST. We are now studying the microstructure of the block copolyesters as well as their potential applications based on the characteristic mechanical properties.

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