ORIGINAL ARTICLE

Preparation of poly(butylene succinate) copolymers including L-aspartic acid

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Copolymers of poly(butylene succinate) (PBS) with amino acids were produced from succinic acid (1), 1,4-butanediol (2) and 1 mol% of various amino acids. Their reaction time and molecular weight, as well as thermal and mechanical properties, were studied. The reaction time for polymerization was found to increase as the amount of amino acid was increased, except when L-aspartic acid (3) was used. The preparation of PBS copolymer including 3 was found to be quite different compared with the preparation of copolymer produced using amino acids. The thermal properties of copolymers including 3 are similar to those of the homopolymer without 3, yet the reaction time, molecular weight distribution and mechanical properties of the copolymers depend significantly on the amount of 3. The reaction time was found to decrease in proportion to the amount of 3. If 3 mol% of 3 is added to the polymerization process, the weight-average molecular weight was found to reach 247 000 in only 15 min. The molecular weight distribution (M_w/M_n) was found to increase and the break strain was found to decrease as the amount of 3 was increased. Similar effects due to the inclusion of 3 were observed in PBS copolymers including ϵ -caprolactone (4) or 3-octadecyloxy-1,2-propanediol (5).

Polymer Journal (2010) 42, 411–415; doi:10.1038/pj.2010.16; published online 24 March 2010

Keywords: amino acid; copolymer; L-aspartic acid; poly(butylene succinate); polyester; reaction time

INTRODUCTION

Aliphatic polyesters such as poly(lactic acid) and poly(butylene succinate) (PBS) receive much attention because they are biodegradable polymers that decompose gradually into carbon dioxide and water. Among all polymers, PBS and its copolymers have superior biodegradability in soil and are now commercially available. Although these polymers exhibit good thermal and mechanical properties, more improvement is needed for other applications. The authors have reported the preparation of various PBS copolymers from succinic acid, 1,4-butanediol and various additional compounds such as monoacylglycerol,¹ 3-alkoxy-1,2-propanediol,² cyclohexanedi-methanol³ and diglycolic acid,⁴ all of which exhibit good mechanical properties.

In this report, PBS copolymers including various amino acids were synthesized and their properties were studied. Among the amino acids, L-aspartic acid exhibited a different reactivity compared with other amino acids. Addition of L-aspartic acid accelerated the polymerization reaction in contrast to the addition of other α -amino acids, which exhibited a delay in polymerization. PBS copolymers, including various amounts of L-aspartic acid, were synthesized and their polymerization time and properties were studied in detail.

EXPERIMENTAL PROCEDURE

Materials

Succinic acid, 1,4-butanediol, titanium tetraisopropoxide, various α -amino acids, ϵ -caprolactone (Wako Pure Chemical, Osaka, Japan) and 3-octadecyloxy-1,2-propanediol (Tokyo Kasei Kogyo, Tokyo, Japan) were used without further purification.

Analysis

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of polymers were determined by gel permeation chromatography (GPC) at a column oven temperature of 40 °C in the Tosoh GPC system SC8020 (Tosoh, Tokyo, Japan) equipped with two TSKgel columns (GHMXL-L) (Tosoh) using an RI detector. Molecular weight calibration was performed according to the polystyrene standard. Chloroform was used as the eluent at a flow rate of 1.0 ml min⁻¹. The compositions of the copolymers were analyzed using ¹H nuclear magnetic resonance spectra measured with a Varian NOVA400 spectrometer (400 MHz) (Varian, Palo Alto, CA, USA).

The thermal properties of polymers, as well as their glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_m), were examined by differential scanning calorimetry (DSC) using a Seiko DSC-220 apparatus (Seiko Instruments, Chiba, Japan). The polymer samples were scanned from –100 to 200 °C at a heating rate of 20 °C per min under a nitrogen stream; T_m , ΔH_m and T_g were determined for second heating. A 2% thermal decomposition temperature (T_{d2}) was determined by thermogravimetry using a Seiko TG/DTA-220 apparatus (Seiko Instruments).

Tensile test

Films (~0.2 mm thick) were prepared using the heat-press method at 200 kg cm⁻², 140 °C. All tensile measurements were performed using a Shimadzu Autograph AGS tester (Shimadzu, Kyoto, Japan) at room temperature. Experiments were carried out at a constant crosshead speed of 10 mm min⁻¹. At least three samples were tested under the same conditions for each polymer, and the average value was calculated.

Preparation of copolymers

The procedure was as follows: a four-necked 100 ml flask was charged with 20.83 g (177 mmol) succinic acid, 16.85 g (187 mmol) 1,4-butanediol, 0.53 g (3.58 mmol) L-aspartic acid and 25 µl (~0.1 mmol) titanium tetraisopropoxide under a dry N₂ atmosphere. The flask, with a gas introduction inlet and outlet and connected to a condenser, was first immersed in a silicon bath. The bath was then heated to 230 °C for 1 h. Water produced by esterification reaction was removed. Subsequently, the condenser was removed and polycondensation was carried out, over a gradually decreasing pressure, for a final vacuum of <1 mm Hg. The reaction was ended after 30 min because the viscosity of the product reached a high enough level to allow the polymer to be twisted around a stirring rod. M_n , M_w and M_w/M_n values of the resulting white solid were determined to be 43 300, 249 400 and 5.76, respectively. T_m , T_g and T_{d2} values of the polymer were determined to be 111.7 °C, -28.8 °C and 299.1 °C, respectively.

RESULTS AND DISCUSSION

PBS copolymers, including amide bond formation, were reported to exhibit good thermal properties.⁵ We tried to produce PBS copolymers including amide bond formation of amino acids because the amino acid is simple to obtain from natural products and has two functional groups: the carboxylic group and the amino group. PBS copolymers, including small amounts of amino acids, can be obtained with high molecular weights from the polycondensation reaction of succinic acid (1), 1,4-butanediol (2) and amino acid. However, larger amounts of amino acids decrease the molecular weight significantly.

Table 1 The reaction time and molecular weight of PBS copolymers including amino acids

Run	Amino acid	Product	Reaction time (h)	M_n	M_w	M_w/M_n
1	None	PBS	3	76 500	142 000	1.86
2	Glycine	PBSGly	7	41 800	74 100	1.78
3	L-Alanine	PBSAla	7	68 400	119 000	1.74
4	L-Aspartic acid	PBSAsp	1.7	46 500	138 000	2.97
5	L-Glutamic acid	PBSGlu	7	37 800	75 700	2.01
6	L-Phenylalanine	PBSPhe	7	58 600	103 000	1.76

Abbreviations: M_n , number-average molecular weight; M_w , weight-average molecular weight; M_w/M_n , molecular weight distribution; PBS, poly(butylene succinate). Succinic acid 180 mmol, 1,4-butanediol 187 mmol and amino acid 1.8 mmol.

Table 1 shows the reaction time under high vacuum, number-average molecular weights (M_n), weight-average molecular weights (M_w) and molecular weight distribution (M_w/M_n) of copolymers when 1 mol% of various amino acids was used for copolymerization. The reaction time for polymerization was increased with the increase in amino acids, except for L-aspartic acid (3).

Table 2 shows the thermal and mechanical properties of the copolymers. 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}), did not change much in the experiments, and were, in general, in agreement with the properties of the PBS homopolymer. The mechanical properties of copolymers, especially the break strain, were varied and were dependent on the type of amino acid used. Copolymers with alanine exhibited a slightly higher break strain than the PBS homopolymer. In this study, 3 was of greater significance because copolymers with 3 exhibited a shorter polycondensation time compared with PBS. PBS and its copolymers generally need a longer reaction time to reach the position of higher molecular weight polymers. Some studies have reported the shortening of polymerization time using chain extension by diisocyanate,^{6–8} the addition of co-catalyst,^{9,10} the addition of three-functional polyols,¹¹ and the use of microwave.¹²

Copolymers of PBS including 3 were prepared (Scheme 1). Table 3 shows the reaction time and molecular weight of PBS copolymers including various amounts of 3. Their thermal and mechanical properties are shown in Table 4. When larger amounts of 3 were used to copolymerize, the reaction time was found to decrease. If 3 mol% of 3 was used for polymerization, it took only 15 min to obtain a copolymer with an M_w of 247 000 (PBSAsp3). The M_w/M_n value of copolymers was found to increase with an increase in 3. The M_w/M_n values of PBS, PBSAsp1, PBSAsp2 and PBSAsp3 were determined to be 1.86, 2.97, 5.76 and 6.71, respectively. Although PBS copolymers including 0.3 mol% of 3 had almost the same reaction time, molecular weight distribution and thermal properties of the PBS homopolymer, the mechanical properties changed. In particular, the break strain increased from 289 to 548%. However, further increases of 3 decreased the break strain significantly—the break strain of PBSAsp3 was only 14% (Table 4, run 2).

It was reported that PBS copolymer including ϵ -caprolactone (4) exhibits superior biodegradability and mechanical properties compared with PBS homopolymer.¹³ Thus, the effect of the addition of aspartic acid to PBS copolymers including 10 mol and 20 mol% of 4 was studied (Scheme 2). Table 5 shows the reaction time and molecular weight of PBS copolymers including 3 and 4. Similar to the results presented in Table 3, the reaction was completed more rapidly. In addition, the molecular weight distribution, M_w/M_n , was found to increase with the increase in 3.

Table 2 The thermal and mechanical properties of PBS copolymers including amino acids

Run	Product	T_g (°C)	T_m (°C)	$-\Delta H_m$ (kJ mg ⁻¹)	T_{d2} (°C)	Elastic (MPa)	Yield stress (MPa)	Break stress (MPa)	Break strain (%)
1	PBS	-34.2	114.9	48.2	308.1	283.8	30.2	30.8	289
2	PBSGly	-34.7	114.9	64.8	325.5	328.3	31.9	30.8	19
3	PBSAla	-30.6	114.4	56.1	328.9	278.4	27.1	33.8	381
4	PBSAsp	-39	109.5	55.4	311.6	280.8	27.9	26.5	38
5	PBSGlu	-30.5	111.4	108	339.1	200.2	27.4	28.7	272
6	PBSPhe	-34.6	113.5	68.5	323.3	295	28.8	28.8	271

Abbreviations: ΔH_m , heat of fusion; PBS, poly(butylene succinate); T_{d2} , 2% thermal decomposition temperature; T_g , glass transition temperature; T_m , melting temperature.

Scheme 1 Polymerization of PBS copolymers including 3.

Table 3 The reaction time and molecular weight of PBS copolymers including aspartic acid

Run	1 (mmol)	2 (mmol)	3 (mmol)	Molar ratio (%) (3/1)	Product	Reaction time	M_n	M_w	M_w/M_n
1	180	188	0	0	PBS	3 h	76 500	142 000	1.86
2	180	187	0.55	0.3	PBSAsp0.3	3 h	80 000	137 000	1.71
3	180	189	1.78	1	PBSAsp1	1.7 h	46 500	138 000	2.97
4	177	187	3.58	2	PBSAsp2	30 min	43 300	249 000	5.76
5	175	187	5.36	3	PBSAsp3	15 min	36 800	247 000	6.71

Abbreviations: M_n , number-average molecular weight; M_w , weight-average molecular weight; M_w/M_n , molecular weight distribution; PBS, poly(butylene succinate); 1, succinic acid; 2, 1,4-butanediol; 3, L-aspartic acid.

Table 4 The thermal and mechanical properties of PBS copolymers including aspartic acid

Run	Product	T_g (°C)	T_m (°C)	$-\Delta H_m$ (mJ mg^{-1})	T_{d2} (°C)	Elastic (MPa)	Yield stress (MPa)	Break stress (MPa)	Break strain (%)
1	PBS	-34.2	114.9	48.2	308.1	283.8	30.2	30.8	289
2	PBSAsp0.3	-30.6	111.1	100	323.3	248	25.1	43.4	548
3	PBSAsp1	-39	109.5	55.4	311.6	280.8	27.9	26.5	38
4	PBSAsp2	-28.8	111.7	107	299.1	276.2	26.3	26.3	20
5	PBSAsp3	-28.6	108.9	108	300.3	279	22.8	22.8	14

Abbreviations: ΔH_m , heat of fusion; PBS, poly(butylene succinate); T_{d2} , 2% thermal decomposition temperature; T_g , glass transition temperature; T_m , melting temperature.

Scheme 2 Polymerization of PBS copolymers including 3 and 4.

Table 6 shows the thermal and mechanical properties of the copolymers. The thermal properties of the copolymers with 3 were not significantly different from those of copolymers without 3. However, the mechanical properties, especially the break strain, changed significantly, depending on the amount of 3. These results are similar to the results presented in Table 4.

PBS copolymers including 3-octadecyloxy-1,2-propanediol (5) exhibit a good break strain level and specific biodegradability;

however, the reaction time of the polymer is long because 5 has a low reactivity.³ The addition effect of 3 to the PBS copolymer including 3 and 5 mol% of 5 was studied (Scheme 3). Table 7 shows the reaction time and molecular weight of PBS copolymers including 3 and 5. The reaction time was found to decrease in proportion to the amount of 3. The M_w/M_n value was found to increase with increasing 3. These results are in agreement with the results of Tables 3 and 5.

Table 5 The reaction time and molecular weight of PBS copolymers including ϵ -caprolactone and aspartic acid

Run	1 (mmol)	2 (mmol)	4 (mmol)	3 (mmol)	Product	Reaction time	M_n	M_w	M_w/M_n
1	180	188	0	0	PBS	3 h	76 500	142 000	1.86
2	180	189	18	0	PBSCL10	4 h	89 800	136 600	1.52
3	180	187	18	0.9	PBSCL10Asp0.5	1.5 h	59 300	142 900	2.41
4	180	189	18	1.8	PBSCL10Asp1	1.5 h	46 800	131 500	2.81
5	180	190	18	5.4	PBSCL10Asp3	20 min	38 800	259 200	6.68
6	180	187	36	0	PBSCL20	4 h	87 200	156 100	1.79
7	180	187	36	0.9	PBSCL20Asp0.5	1.3 h	58 800	140 500	2.39
8	181	187	36	1.8	PBSCL20Asp1	1 h	53 600	187 100	3.49
9	180	187	36	5.4	PBSCL20Asp3	10 min	35 300	289 500	8.20

Abbreviations: M_n , number-average molecular weight; M_w , weight-average molecular weight; M_w/M_n , molecular weight distribution; PBS, poly(butylene succinate); 1, succinic acid; 2, 1,4-butanediol; 3, L-aspartic acid; 4, ϵ -caprolactone.

Table 6 The thermal and mechanical properties of PBS copolymers including ϵ -caprolactone and aspartic acid

Run	Product	T_g (°C)	T_m (°C)	$-\Delta H_m$ (mJ mg ⁻¹)	T_{d2} (°C)	Elastic (MPa)	Yield stress (MPa)	Break stress (MPa)	Break strain (%)
1	PBS	-34.2	114.9	48.2	308	283.8	30.2	30.8	289
2	PBSCL10	-34.3	105.2	71.9	331.3	142.9	24.7	26.3	291
3	PBSCL10Asp0.5	-21.1	107.4	57.5	320.3	134.6	25	23.2	257
4	PBSCL10Asp1	-35	102.9	95.8	300.9	141.5	24.4	24.2	21
5	PBSCL10Asp3	-32.6	101.6	75.1	300.7	133	24	23.8	19
6	PBSCL20	-36.3	100.9	49.7	322	116.5	20.2	47.4	1102
7	PBSCL20Asp0.5	-38	98	59.7	321.1	100.5	18.6	20	306
8	PBSCL20Asp1	-36	98.2	79.4	302.3	115.4	19.9	19.2	196
9	PBSCL20Asp3	-35.7	96	61.7	299.3	107.5	19.2	17.9	27

Abbreviations: ΔH_m , heat of fusion; PBS, poly(butylene succinate); T_{d2} , 2% thermal decomposition temperature; T_g , glass transition temperature; T_m , melting temperature.

Scheme 3 Polymerization of PBS copolymers including 3 and 5.

Table 8 shows the thermal and mechanical properties of the copolymers, which is consistent with the results presented in Tables 4 and 6—the break strain was found to decrease with increasing amounts of 3.

It was found that the addition of 3 was effective in accelerating the polymerization of PBS and its various copolymers. It was suggested that this is due to the three functional groups of 3, two carboxylic groups and an amino group, producing a network polymer. A similar acceleration effect has been reported for three-functional polyols.¹¹ However, L-glutamic acid, which has a structure that is similar to 3, produced the same behavior as other amino acids that had two functional groups. This means that there is another reason for the specific results linked to 3.

CONCLUSION

PBS copolymers including 1 mol% of amino acid were produced at high molecular weights and good break strain. However, if the amount of amino acid except for 3 was increased, a high-molecular-weight copolymer could not be obtained. In contrast, PBS copolymers, including small amounts of 3, were prepared over a short reaction time with high weight-average molecular weight. The molecular weight distribution of the copolymer was found to increase, whereas the break strain was found to decrease with an increase in 3. PBS copolymers including 4 and 5 could also be obtained over a shorter time with high M_w and high M_w/M_n with the addition of 3. These results are considered to be attributed to the three functions of 3; an

Table 7 The reaction time and molecular weight of PBS copolymers including 3-octadecyloxy-1,2-propanediol and aspartic acid

Run	1 (mmol)	2 (mmol)	5 (mmol)	3 (mmol)	Product	Reaction time	M _n	M _w	M _w /M _n
1	180	188	0	0	PBS	3 h	76 500	142 000	1.86
2	181	181	5.5	0	PBSODP3	6.5 h	117 700	203 800	1.73
3	181	181	5.4	1	PBSODPAsp0.5	5 h	69 800	142 900	2.05
4	180	182	5.4	2	PBSODP3Asp1	2 h	47 000	119 000	2.52
5	181	184	5.1	3.6	PBSODP3Asp2	15 min	39 600	296 800	7.5
6	180	177	9	0	PBSODP5	7 h	97 100	187 800	1.94
7	180	177	9.1	1.8	PBSODP5Asp1	3 h	59 000	132 300	2.24
8	180	177	9	3.6	PBSODP5Asp2	45 min	46 300	294 400	6.36

Abbreviations: M_n, number-average molecular weight; M_w, weight-average molecular weight; M_w/M_n, molecular weight distribution; PBS, poly(butylene succinate); 1, succinic acid; 2, 1,4-butanediol; 3, L-aspartic acid; 5, 3-octadecyloxy-1,2-propanediol.

Table 8 The thermal and mechanical properties of PBS copolymers including 3-octadecyloxy-1,2-propanediol and aspartic acid

Run	Product	T _g (°C)	T _m (°C)	−ΔH _m (mJ mg ^{−1})	T _{d2} (°C)	Elastic (MPa)	Yield stress (MPa)	Break stress (MPa)	Break strain (%)
1	PBS	−34.2	114.9	48.2	308.1	283.8	30.2	30.8	289
2	PBSODP3	−26.7	111.5	88.3	325.7	156.8	23	52	898
3	PBSODPAsp0.5	−28.7	111	86.3	325	133	22.9	38.4	630
4	PBSODP3Asp1	−30.2	108.4	101	306	136.2	23.5	21.7	74
5	PBSODP3Asp2	−26.9	109.8	110	297.7	156.3	28.9	28.8	19
6	PBSODP5	−27.1	107.9	84.2	328.1	109.5	19.3	44.8	903
7	PBSODP5Asp1	−25.9	109.2	94.7	315.1	115.4	19.6	27.4	496
8	PBSODP5Asp2	−25.4	107.3	89.7	312.9	106.3	20.3	18.1	52

Abbreviations: ΔH_m, heat of fusion; PBS, poly(butylene succinate); T_{d2}, 2% thermal decomposition temperature; T_g, glass transition temperature; T_m, melting temperature.

explanation for the different behaviors between 3 and L-glutamic acid has not been found.

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