

Synthesis of Poly(butylene succinate) and Poly(ethylene succinate) Including Diglycollate Moiety

Akihiro OISHI, Min ZHANG, Kazuo NAKAYAMA, Takashi MASUDA, and Yoichi TAGUCHI[†]

*National Institute of Advanced Industrial Science and Technology (AIST),
Central 5, 1-1-1, Higashi, Tsukuba 305-8565, Japan*

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ABSTRACT: Poly(butylene succinate) (PBS) copolymers were prepared from succinic acid, diglycollic acid, and 1,4-butanediol, in the presence of titanium tetraisopropoxide and magnesium hydrogen phosphate trihydrate. All the polymers produced exhibited a higher number-average molecular weight than 65,000. The composition of the copolymers was found to be almost the same as the feed composition. The copolymers exhibited a higher break strain compared to the homopolymer. The biodegradability of copolymers showed a maximum when 2% diglycollic acid was added. However, the addition of more diglycollic acid decreased biodegradability. Poly(ethylene succinate) (PES) copolymers, including diglycollate moiety, were also prepared from succinic acid, diglycollic acid, and ethylene glycol, using the same reaction conditions as the PBS copolymers. Unlike the PBS copolymers, the molecular weights of the PES copolymers decreased for an increasing amount of diglycollate while the biodegradability rose with an increase of the diglycollate ratio in the copolymers, in the range 0–20%. [doi:10.1295/polymj.PJ2005206]

KEY WORDS Poly(butylene succinate) / Poly(ethylene succinate) / Diglycollic Acid / Copolymerization / Break Strain / Biodegradation /

Much attention has been paid to biodegradable polymers for the production of environmentally friendly plastics. Such plastics would eventually decompose into carbon dioxide and water in nature. It is well known aliphatic polyesters are good biodegradable polymers and exhibit many excellent properties.^{1–4} Poly(butylene succinate) (PBS), an aliphatic polyester, exhibits good thermal and mechanical properties similar to polyethylene and polypropylene. The improvement of the PBS properties has been widely investigated by many scientists.^{5–7}

Recently, we reported the preparation of various PBS copolymers from succinic acid, 1,4-butanediol and various additional compounds, such as ϵ -caprolactone,⁷ monoacylglycerol,⁸ 3-alkoxy-1,2-propanediol⁹ and cyclohexane dimethanol.¹⁰ The copolymer including 5 mol % 3-octadecyloxy-1,2-propanediol exhibited a high break strain of 833%, whereas the biodegradation rate of the copolymer was slower than the homopolymer.⁹

In this report, PBS copolymers, including diglycollic acid, were synthesized and their properties were studied. Although diglycollic acid (2) has a similar structure to succinic acid (1), it possesses ether-oxygen in molecules and thus, thermal, mechanical and biodegradable properties are expected to be different. The synthesis of poly(ethylene succinate) (PES), including diglycollic acid, and its properties were also studied.

EXPERIMENTAL

Materials

Succinic acid (1), 1,4-butanediol (3), titanium tetraisopropoxide, magnesium hydrogen phosphate trihydrate and diglycollic acid (Wako Pure Chemical) were used without further purification. Commercial compost soil (Tokawa Heiwa Noen) was purchased for the biodegradation test.

Tensile Test

Films (about 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 TOYO BALDWIN SS-207-EP tester at room temperature. Experiments were performed at a constant crosshead speed of 10 mm/min. At least three samples were tested under the same conditions for each polymer. The average value was estimated.

Degradation of Polymers

Films of initial dimension 25 × 25 × 0.2 mm were placed in compost soil at 30 °C and 95% moisture. The films were removed at regular intervals, washed with distilled water and dried to constant weight in vacuum before analysis. For each test, three films were used and the average value of their weight-loss amounts was taken as the final result.

[†]To whom correspondence should be addressed (Tel: +81-29-861-4576, Fax: +81-29-861-4576, E-mail: y-taguchi@aist.go.jp).

Table I. M_n and M_w/M_n of PBS copolymers including diglycolic acid (1)^a

Run	1 mmol	2 mmol	3 mmol	1/2 ^b	Product	M_n^c	M_w/M_n^c
1	180	0	198	100/0	PBS	86,300	1.97
2	178	2	198	99/1	PBSDG1	89,600	2.06
3	176	4	198	98/2	PBSDG2	84,500	2.08
4	171	9	198	95/5	PBSDG5	80,100	2.19
5	162	18	198	90/10	PBSDG10	75,600	2.09
6	144	45	198	80/20	PBSDG20	79,200	2.05
7	90	90	198	50/50	PBSDG50	67,900	2.02
8	36	144	198	20/80	PBSDG80	65,400	1.96
9	0	180	198	0/100	PBDG	79,600	1.96

^aTi(O-*i*-Pr)₄ 0.116 mmol, MgPO₄·3H₂O 0.04 mmol, 230 °C, reaction time 1–1.5 h. ^bMolar ratio. ^cDetermined by GPC.

Preparation of Copolymers

The typical procedure was as follows: a four-necked 100 mL flask was charged with 20.18 g (171 mmol) succinic acid, 17.82 g (198 mmol) 1,4-butanediol, 1.21 g (9.0 mmol) diglycolic acid, 0.030 g (0.12 mmol) titanium tetraisopropoxide and 0.0069 g (0.04 mmol) magnesium hydrogen phosphate trihydrate under dry N₂ atmosphere. The flask, with a gas introduction inlet and outlet, connected to a condenser was first immersed in a silicon oil bath preset at 230 °C, then heated, to remove the esterification reaction by-product of water, for 1 h. Subsequently, the condenser was removed and polycondensation was carried out, over a gradually decreasing pressure, for a final vacu-

um of less than 0.1 mmHg. Polycondensation was concluded once the viscosity of the product reached high enough to twist around stirring rod.

RESULTS AND DISCUSSION

The synthesis of PBS copolymers, including diglycolate moiety, was carried out from succinic acid (1), diglycolic acid (2), and 1,4-butanediol (3), using titanium tetraisopropoxide as the catalyst. Furthermore, magnesium hydrogen phosphate was also used in the reaction as a co-catalyst because it has an acceleration effect in the synthesis of PBS.¹¹

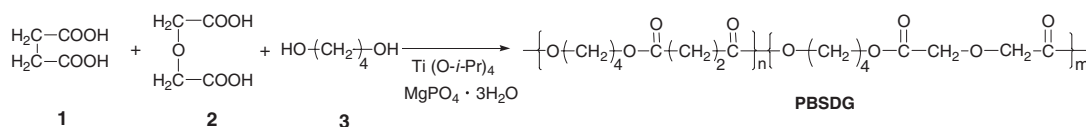


Table I shows number-average molecular weights (M_n) and the molecular weight distribution (M_w/M_n) of obtained polymers. An M_n higher than 65,000 was obtained for all polymers. The M_w/M_n ratio of the polymers was found to be between 1.96 and 2.19.

Figure 1 is the ¹H NMR spectrum of PBSDG50: the compositions of 1 and 2 in the copolymers were estimated from the ratio of the methylene proton resonance intensities of Hb or Hc, and Hd or He, with respect to the intensity of Ha. The results of the estimate are given in Table II. The compositions of the 1 and 2 moieties in the copolymers were almost the same as the feed compositions of 1 and 2.

In Table III the thermal properties of the copolymers are presented: the glass transition temperature (T_g) increases and the melting temperature (T_m) decreases with an increase of 2 in the copolymers. These trends are as expected with the PBS copolymers containing monoacylglycerol⁸ and 3-alkoxy-1,2-propanediol.⁹

In Table IV the tensile tests of the produced polymers are presented: the values of elastic modulus, yield stress, and break stress decrease as the ratio of 2 in the copolymers increases and become negligible at PBSDG50 and PBSDG80. PBS copolymers containing 3-alkoxy-1,2-propanediol exhibit a higher break strain than the PBS homopolymer.⁹ Copolymers in Table IV also exhibit a higher break strain than PBS and PBDG.

In Figure 2 the biodegradation experimental results of PBS, PBSDG2, PBSDG5, PBSDG10, PBSDG20, PBSDG50, and PBDG, in commercial compost soil under 30 °C and 95% RH, are presented. The weight loss of PBS by hydrolysis in air under the same conditions was scarcely detected in 8 weeks. Biodegradability was thus expressed as the weight loss, as a function of buried time, for 25 × 25 × 0.2 mm films. PBSDG2 achieved the maximum biodegradability. However, the biodegradability decreases as the ratio of 2 in the copolymers increases. PBDG, a polymer

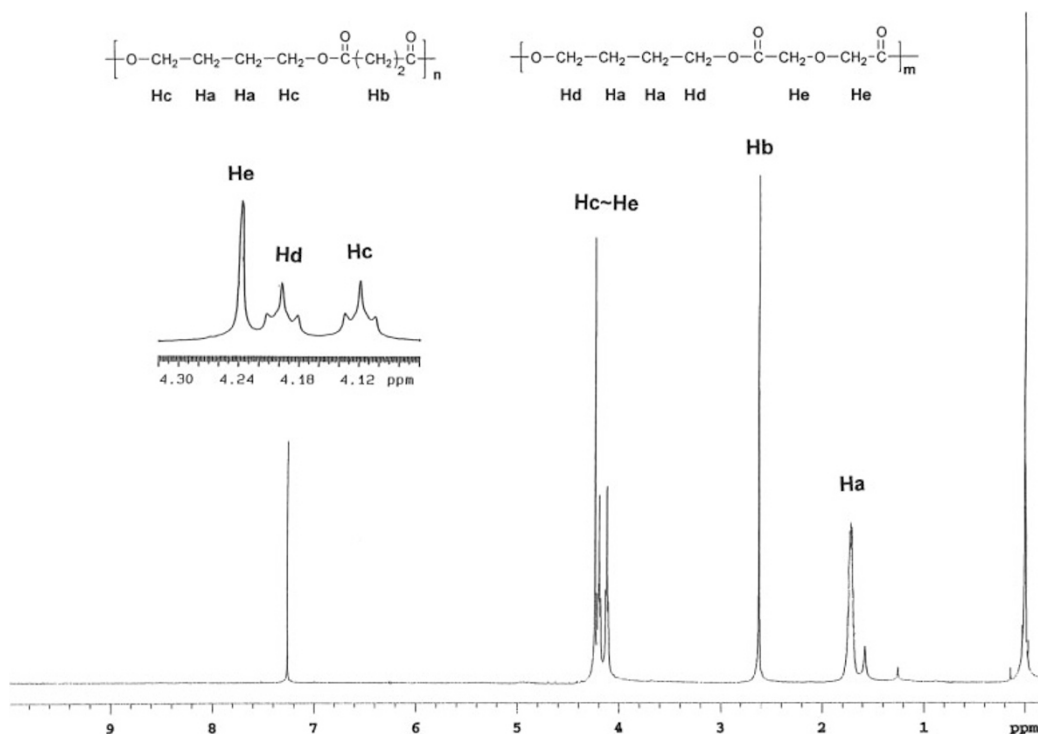


Figure 1. ^1H NMR spectrum of PBSDG50.

Table II. The ratio of components of succinate and diglycolate in copolymers by NMR analysis

Monomer	1/2	The ratio of succinate (%)		The ratio of diglycolate (%)	
		Hb/Ha	Hc/Ha	Hd/Ha	He/Ha
PBS	100/0	101	99	0	0
PBSD1	99/1	99	99	1	3
PBSDG2	98/2	99	98	1	5
PBSDG5	95/5	96	95	5	5
PBSDG10	90/10	90	90	10	9
PBSDG20	80/20	78	79	20	19
PBSDG50	50/50	46	51	47	48
PBSDG80	20/80	18	21	75	82
PBDG	0/100	0	0	95	98

Table III. Thermal properties of PBS copolymers including diglycolic acid

Product	T_g °C	T_m °C	ΔH_m mJ/mg	Td2 °C
PBS	-35.7	112	128	304
PBSD1	-34.3	114	105	311
PBSDG2	-33.9	114	110	312
PBSDG5	-34.6	111	112	318
PBSDG10	-31.9	106	94	312
PBSDG20	-37.5	95	97	309
PBSDG50	-35.0	55	43	318
PBSDG80	-29.9	47	57	326
PBDG	-27.2	59	68	321

Table IV. Mechanical properties of PBS copolymers including diglycolic acid

Product	Elastic MPa	Yield Stress MPa	Break Stress MPa	Break Strain %
PBS	301.0	29.3	29.3	210.3
PBSD1	268.8	29.4	48.7	589.2
PBSDG2	274.3	27.1	30.8	292.5
PBSDG5	268.4	24.7	45.2	604.9
PBSDG10	231.3	21.8	26.8	360.4
PBSDG20	178.7	17.2	32.1	610.2
PBSDG50	1.8	6.4	19.1	921.0
PBSDG80	2.2	6.2	15.5	542.4
PBDG	86.7	13.0	31.7	512.8

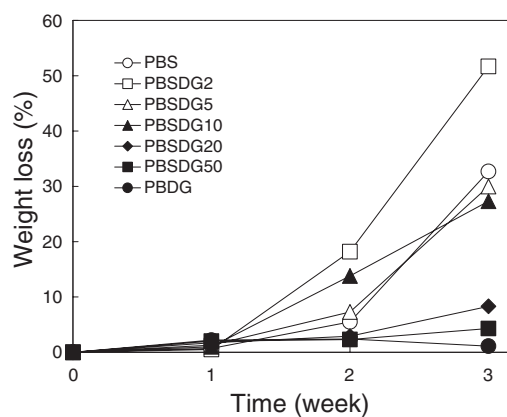


Figure 2. Buried time dependence of biodegradation of PBS copolymers.

Table V. M_n and M_w/M_n of PES copolymers including diglycollic acid^a

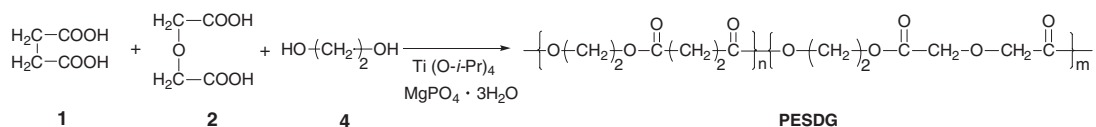
Run	1 mmol	2 mmol	3 mmol	1/2 ^b	Product	M_n^c	M_w/M_n^c
1	180	0	198	100/0	PES	72,300	2.09
2	178	2	198	99/1	PESDG1	76,900	2.20
3	176	4	198	98/2	PESDG2	79,800	1.99
4	171	9	198	95/5	PESDG5	72,700	2.08
5	162	18	198	90/10	PESDG10	65,300	2.16
6	144	45	198	80/20	PESDG20	52,700	1.83
7	90	90	198	50/50	PESDG50	42,800	2.79
8	36	144	198	20/80	PESDG80	37,400	3.18
9	0	180	198	0/100	PEDG	30,500	2.17

^aTi(O-*i*-Pr)₄ 0.116 mmol, MgPO₄·3H₂O 0.04 mmol, 230 °C, reaction time 1–1.5 h. ^bMolar ratio. ^cDetermined by GPC.

obtained from 2 and 3, exhibits no biodegradability under our test conditions.

The synthesis of poly(ethylene succinate) (PES) copolymers, including diglycollate moiety, was also studied. PES and its copolymers have also been reported to be biodegradable.^{12,13} Although the synthesis of PES, *via* ring-opening polymerization of succin-

ic anhydride and ethylene oxide^{12,14} or by polycondensation of dimethyl succinate and ethylene glycol,¹⁵ has been reported, the molecular weights were not high enough. In our experiment PES with a high molecular weight was synthesized using the same polycondensation as in the synthesis of the PBS copolymers.



In Table V the number-average molecular weights (M_n) and the molecular weight distribution (M_w/M_n) of PES copolymers are presented. Copolymers with an M_n higher than 60,000 could be obtained at 0–10 mol % of 2. Unlike PBS copolymers, the M_n of the copolymers decreased with an increasing amount of 2. The M_n of PEDG, a polymer obtained from 2 and 4, decreased to 30,500. M_w/M_n of PESDG50 and PESDG80 was higher than others. The reason was presumed that a part of the copolymers depolymerized.

Figure 3 is the ¹H NMR spectrum of PESDG50: the composition of 1 and 2 in the copolymers were estimated from the ratio of the methylene proton resonance intensity of H_b with respect to the intensity of H_a. The results are presented in Table VI. The composition of 1 and 2 in all copolymers was almost the same as the feed composition of 1 and 2. This result is in agreement with the PBS copolymers (Table II).

In Table VII the thermal properties of the synthesized copolymers are presented. The melting temperature (T_m) was not measured using the DSC measurement of the copolymers that include more than 5% of 2. The loss of the DSC peak can be attributed to the amorphousness of the copolymers. The same phenomenon is also observed for the poly(BS-co-ES) copolymers.¹³

In Table VIII the results of the tensile tests of the synthesized polymers are presented. PESDG10 and PESDG20 exhibit a higher break strain than the PES homopolymer. The results are agreement with the tendency of PBS copolymers (Table IV). However, data of PESDG50, PESDG80, and PEDG could not be measured because it was extremely difficult to prepare films. The reason was presumed because of their lower molecular weights and amorphousness.

In Figure 4 the experimental biodegradation results of PES, PESDG1, PESDG2, PESDG5, PESDG10, and PESDG20 are presented: the biodegradability rises as the ratio of 2 in the copolymers increases in the range of these compositions. The biodegradability of PES copolymers was much lower than that of the PBS copolymers in these experiments.

CONCLUSION

PBS copolymers with an M_n higher than 65,000, including diglycollate, were obtained *via* the reactions of 1, 2, and 3. The compositions of the copolymers were almost the same as the feed compositions. However, the values of the elastic modulus, yield stress and break stress decreased. The break strain increased with an increase of 2. The biodegradability of copolymers peaks at a 2% diglycollate ratio, but decreases

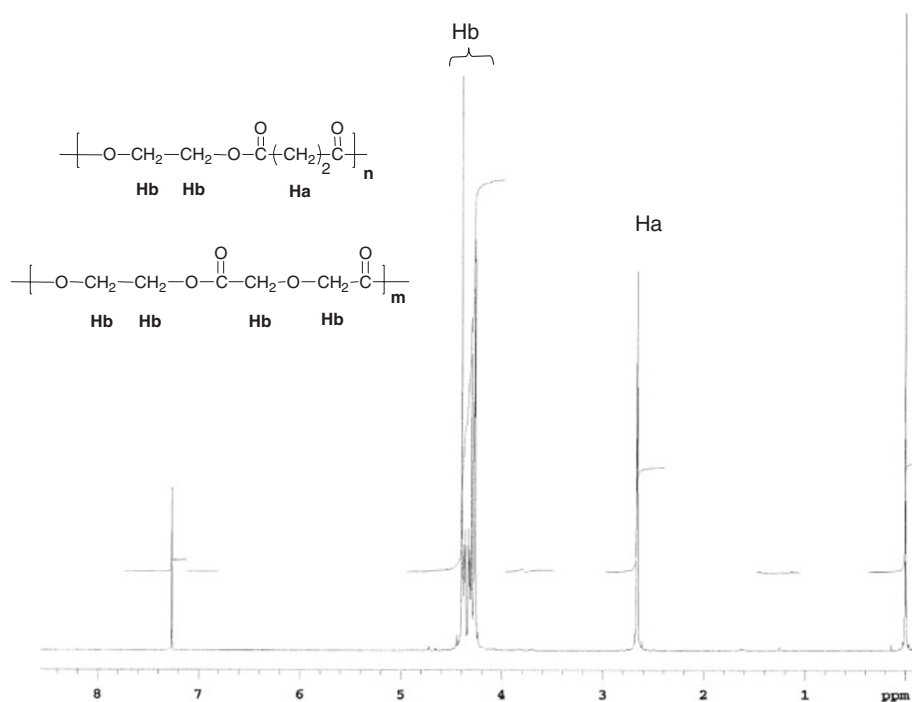


Figure 3. ¹H NMR spectrum of PESDG50.

Table VI. The ratio of components of succinate and diglycolate by NMR analysis

	Monomer	The ratio of diglycolate (%)
	1/2	(Ha - Hb)/(Ha + Hb)
PES	100/0	0
PESDG1	99/1	1.5
PESDG2	98/2	2.1
PESDG5	95/5	5.0
PESDG10	90/10	10.5
PESDG20	80/20	21.0
PESDG50	50/50	58.4
PESDG80	20/80	87.7
PEDG	0/100	100

Table VIII. Mechanical properties of PES copolymers including diglycolic acid

Product	Elastic MPa	Yield Stress MPa	Break Stress MPa	Break Strain %
PES	383.6	23.8	33.8	439.0
PESD1	351.0	22.2	44.6	676.0
PESDG2	321.5	21.8	28.6	422.9
PESDG5	235.4	20.4	38.7	716.0
PESDG10	215.0	17.5	39.0	834.3
PESDG20	109.5	11.7	21.5	859.2
PESDG50	×	×	×	×
PESDG80	×	×	×	×
PEDG	×	×	×	×

Table VII. Thermal properties of PES copolymers including diglycolic acid

Product	T_g °C	T_m °C	ΔH_m mJ/mg	Td2 °C
PES	-10.6	99.6	88	299
PESD1	-10.5	98.0	78	295
PESDG2	-9.6	97.9	55	296
PESDG5	-10.3	92.0	×	311
PESDG10	-10.1	×	×	305
PESDG20	-8.5	×	×	300
PESDG50	-3.9	×	×	305
PESDG80	1.2	×	×	305
PEDG	3.2	×	×	312

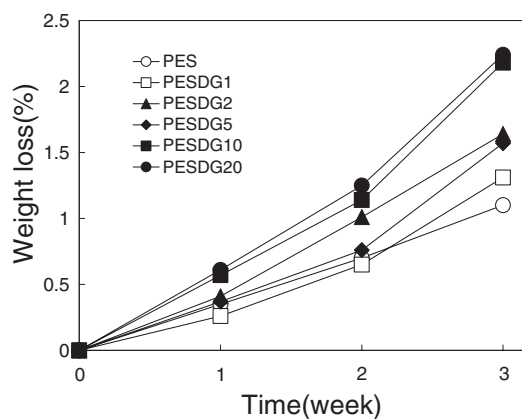


Figure 4. Buried time dependence of biodegradation of PES copolymers.

with a further rise in the diglycollate ratio. This result suggests that there is the possibility of biodegradability control based on the amount of 2.

PES copolymers, including diglycollate, that exhibit a high molecular weight could also be obtained from the reaction of 1, 2, and 4. It was found that the molecular weights of the copolymers decreased as the ratio of 2 increased. The compositions of the copolymers were the same as the feed compositions. The biodegradability of the copolymers rose with an increase in the ratio of 2.

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