Copolymerization of Poly(butylene succinate) with 3-Alkoxy-1,2-propanediols

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ABSTRACT: A copolymer of poly(butylene succinate) was produced from dimethyl succinate (**1**), 1,4-butanediol (**2**) and 3-alkoxy-1,2-propanediol (**3**) such as 3-methoxy-1, 2-propanediol (**3a**), 3-allyloxy-1, 2-propanediol (**3b**) and 3-octadecyloxy-1, 2-propanediol (**3c**). Copolymers of high molecular weight were obtained when a small amount of **3** was included, but molecular weight decreased with increasing amount of **3**. Copolymers including a small amount of **3** had larger break strain than homopolymer. Although the copolymer including 0.3% **3c** possessing an alkyl long chain had the largest break strain, copolymers including more amount of **3c** had lower molecular weights and lower break strain because of the low reactivity of secondary alcohol of **3c**. To accelerate copolymerization a new method was designed in which diols of **3c** are first esterified by succinic anhydride and then copolymerization. When 0–5 mol% of **3c** was used in copolymerization by the method, copolymers with M_n higher than 60000 were obtained. The copolymer including 5 mol% of **3c** showed break stress reached of 833%, and the biodegradation rate of the copolymer was slower than homopolymer.

KEY WORDS Poly(butylene succinate) / 3-Alkoxy-1, 2-propandiol / 3-Octadecyloxy-1, 2-propanediol / Copolymer / Break Strain / Biodegradation /

Much attention has been paid to biodegradable polymers for environmentally friendly plastics. They finally decompose into carbon dioxide and water in nature. Aliphatic polyesters are good biodegradable polymers and have many excellent properties.^{1–4} Poly(butylene succinate) (PBS), an aliphatic polyester, has good thermal and mechanical properties similar to polyethylene and polypropylene. Improvement of PBS properties has been widely investigated by many scientists.^{5–7}

Recently, we reported that PBS copolymerized with monoacylglycerol was produced from dimethyl succinate, 1,4-butanediol and monoacylglycerol such as monolaurin, monostearin, and monoolein.⁸ The break stress of the copolymer containing 0.3 mol% monostearin or monoolein to dimethyl succinate was three times that of the PBS homopolymer, though the number average molecular weight and thermal properties of copolymer were the same as those of the homopolymer. But, at more than 1 mol% monoacylglycerol to dimethyl succinate for copolymerization, gelation occurred and the copolymers were insoluble in chloroform owing to transesterification of a portion of the monoacylglycerol component.

New copolymers including 3-alkoxy-1,2-propanediol such as 3-methoxy, 3-allyloxy, and 3-octadecyloxy-1,2-propanediol were synthesized, and thermal, me-

chanical, and biodegradable properties of copolymers were studied.

EXPERIMENTAL

Materials

Dimethyl succinate (**1**), 1,4-butanediol (**2**), titanium tetraisopropoxide (Wako Pure Chemical), 3-methoxy-1,2-propanediol (**3a**), 3-allyloxy-1,2-propanediol (**3b**) and 3-octadecyloxy-1,2-propanediol (**3c**) (Tokyo Kasei Kogyo) were used without further purification. Commercial compost soil (Tokawa Heiwa Noen) was purchased for biodegradation test.

Analysis

The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of polymers were determined by gel permeation chromatography (GPC) at column oven temperature 40 °C on a Tosoh GPC system SC8020 equipped with two TSKgel columns (GMHXL-L) using RI detector. Molecular weight was calibrated according to polystyrene standard. Chloroform was used as eluent at a flow rate of 1.0 mL min⁻¹.

The compositions of copolymers were analyzed by ¹H NMR spectra measured on a Varian Gemini 300BB spectrometer (300 MHz).

The thermal properties of polymers, glass transition

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Scheme 1.

temperature (T_g), melting temperature (T_m), and heat of fusion (ΔH_m) were examined by differential scanning calorimetry (DSC) on a Seiko DSC-220 apparatus, and 2% thermal decomposition temperature (Td2) was determined by thermogravimetry on Seiko TG/DTA-220 apparatus. Polymer samples were scanned from -100 to 200°C at a heating rate of $20^\circ\text{C min}^{-1}$ under nitrogen stream. T_m , ΔH_m , and T_g was determined in the second heating.

Tensile Test

Films (about 0.2 mm thick) were prepared by the heat-press method at 200 kg cm^{-2} and 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^{-1} . A least of three samples were tested under the same conditions for each polymer, and the average value was taken as representative.

Degradation of Polymers

Films of initial dimension $25 \times 25 \times 0.2\text{ mm}$ 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 sample, three films were used and average weight-loss amount was taken as the result.

Preparation of Copolymers

A typical procedure was as follows. A three-necked 100 mL flask was charged with 180 mmol dimethyl succinate, 187 mmol 1,4-butanediol, 0.54 mmol 3-octadecyloxy-1,2-propanediol and 0.10 mmol titanium tetraisopropoxide under dry N_2 atmosphere. The flask

provided with a gas introduction inlet and outlet connected with a condenser was first immersed in a silicon oil bath preset at 215°C , and heated to remove the esterification reaction byproduct of methanol for 1 h . Subsequently, the condenser was removed, and polycondensation was carried out under gradually reduced pressure with a final degree of vacuum less than 0.1 mmHg . Polycondensation was ended when the viscosity of the product was high enough.

RESULTS AND DISCUSSION

Copolymers of PBS with monoacylglycerol show higher break strain than PBS homopolymer, but gelation based on the transesterification of monoacylglycerol takes place.⁸ Although 3-alkoxy-1,2-propanediols bear close resemblance to monoacylglycerol, they do not transesterificate owing to have ether bonds instead of ester bonds of monoglyceride. 3-Alkoxy-1,2-propanediol instead of monoacylglycerol should thus improve the break strain of PBS copolymers without gelation. So the synthesis of PBS copolymers was carried out from dimethyl succinate (**1**), 1,4-butanediol (**2**), and 3-alkoxy-1,2-propanediol (**3**) such as 3-methoxy-1,2-propanediol (**3a**), 3-allyloxy-1,2-propanediol (**3b**), and 3-octadecyloxy-1,2-propanediol (**3c**).

Table I shows number-average molecular weights (M_n) and molecular weight distribution (M_w/M_n) of copolymers including **3a**, **3b**, and **3c**. High molecular weight copolymers were obtained when a small amount of **3** was added. Molecular weights of copolymers decreased with increasing amount of **3** (Runs 5, 9, and 13), and only $1\text{ mol\%}$ of **3c** having an alkyl long chain

Table I. M_n and M_w/M_n of copolymers including 3-alkoxy-1,2-propanediol^a

Run	1 mmol	2 mmol	3	R	mmol	3/1 ^b %	Copolymer	M_n^c	M_w/M_n^c
1	180	188	None			0.0	PBS1	32400	1.63
2	180	186	3a	Methyl	0.54	0.3	PBSM(0.3)	68500	1.99
3	180	185	3a	Methyl	1.99	1.0	PBSM(1)	62500	2.05
4	180	185	3a	Methyl	3.67	2.0	PBSM(2)	49200	1.60
5	180	171	3a	Methyl	9.06	5.0	PBSM(5)	33800	1.32
6	180	186	3b	Allyl	0.84	0.5	PBSA(0.5)	71300	2.17
7	180	185	3b	Allyl	1.76	1.0	PBSA(1)	79000	2.15
8	180	186	3b	Allyl	3.60	2.0	PBSA(2)	63500	2.11
9	180	171	3b	Allyl	9.10	5.0	PBSA(5)	35900	1.78
10	180	187	3c	Octadecyl	0.38	0.2	PBSO(0.2)	63700	1.75
11	180	187	3c	Octadecyl	0.54	0.3	PBSO(0.3)	68900	1.65
12	180	187	3c	Octadecyl	0.95	0.5	PBSO(0.5)	43600	1.40
13	180	186	3c	Octadecyl	1.80	1.0	PBSO(1)	22900	1.53

^aTi(O-*i*-Pr)₄ 0.1 mmol, 215 °C, reaction time 3–6 h. ^bMolar ratio. ^cDetermined by GPC.**Table II.** Thermal properties of copolymers

Run	Copolymer	T_g (°C)	T_m (°C)	ΔH_m (mJ mg ⁻¹)	Td2
1	PBS1	-39.9	114.1	110.1	322.2
2	PBSM(0.3)	-34.8	114.9	69	299.3
3	PBSM(1)	-38.1	115.3	80.10	309.9
4	PBSM(2)	-35.2	113.7	76.10	299.8
5	PBSM(5)	-35.3	113	65.00	309.9
6	PBSA(0.5)	-36.6	114.9	72.4	303.2
7	PBSA(1)	-43.2	111.9	75.40	309.9
8	PBSA(2)	-37.6	114.1	71.70	304.3
9	PBSA(5)	-39.1	111.9	76.60	317.7
10	PBSO(0.2)	-35.2	114.1	100.7	300.9
11	PBSO(0.3)	-41.9	114.9	82.30	313.0
12	PBSO(0.5)	-39.9	114.9	85.40	311.8
13	PBSO(1)	-43.5	114.9	93.50	283.5

lowered M_n of the copolymer. The cause was considered the low reactivity of secondary alcohol of **3**.

Table II shows the thermal properties of the obtained copolymers. Glass transition temperature (T_g) and melting temperature (T_m) did not changed much in the experiments. This means that the copolymers have the almost same thermal properties.

Table III shows the tensile tests of obtained copolymers. PBS copolymers including 0.3% and 0.5% of monoacylglycerol have larger break strain than PBS homopolymer.⁸ Also in Table III, copolymers **PBSM(0.3)**, **PBSM(1)**, **PBSM(2)**, **PBSA(0.5)**, **PBSA(1)**, **PBSA(2)**, **PBSO(0.2)**, **PBSO(0.3)**, and **PBSO(0.5)** have larger break strain than homopolymer, **PBS1**. But **PBSM(5)**, **PBSA(5)**, and **PBSO(1)** were very brittle and had small break strain. It was considered that the cause of brittleness was the small molecular weight of copolymers.

Figure 1 shows the relationship between added **3** and break strain. **PBSO(0.3)** which is the copolymer including 0.3 mol% of **3c** had the largest break strain of 469.9%. **PBSO(0.5)** and **PBSO(1)** including more **3c**

Figure 1. Break strain of copolymers including 3-alkoxy-1,2-propanediol.

lowered the break strain. The cause was considered that the low reactivity of secondary alcohol of **3c** decreased the M_n . So a method was designed in which diols of **3c** are esterified at first by succinic anhydride and then copolymerization reaction is carried out (Scheme 2).

Table III. Tensile strength of copolymers

Run	Copolymer	Elastic MPa	Yield Stress MPa	Break Stress MPa	Break Strain %
1	PBS1	333	32.4	29.9	119.3
2	PBSM(0.3)	292	26.6	29.8	277.6
3	PBSM(1)	500	22.9	59.5	303.1
4	PBSM(2)	317	26.7	35.3	371.6
5	PBSM(5)	319	26.4	27.30	20.0
6	PBSA(0.5)	274	26.3	34.3	323.5
7	PBSA(1)	472	21.9	55.8	289.4
8	PBSA(2)	309	27.3	32.7	305.3
9	PBSA(5)	329	25.7	26.10	43.1
10	PBSO(0.2)	308	28.0	34.9	355.8
11	PBSO(0.3)	277	24.7	40.3	469.9
12	PBSO(0.5)	269	27.1	26.1	166.9
13	PBSO(1)	brittle	x	x	x

Scheme 2.**Table IV.** M_n and M_w/M_n of copolymers including 3-octadecyloxy-1,2-propanediol^a

Run	1 mmol	4 mmol	2 mmol	3c mmol	$3c/(1+4)^b$ (%)		Copolymer	M_n^c	M_w/M_n^c
					Feed	Copolymer			
1	130	50	187	0	0	0	PBS2(0)	69400	1.90
2	130	50	189	0.54	0.3	obscure	PBS2(0.3)	97100	2.07
3	130	50	188	0.90	0.5	obscure	PBS2(0.5)	78200	1.91
4	130	50	188	1.8	1.0	1.6	PBS2(1)	64300	1.86
5	130	50	188	3.6	2.0	2.6	PBS2(2)	98300	1.74
6	130	50	188	9.0	5.0	5.9	PBS2(5)	71800	1.77
7	130	50	170	18.0	10.0	11.5	PBS2(10)	31200	1.70

^aTi(O-*i*-Pr)₄ 0.1 mmol, 215 °C, reaction time 3–6 h. ^bMolar ratio. ^cDetermined by GPC.

Table IV shows the M_n and M_w/M_n of the copolymers synthesized by the new method. This method accelerated polymerization and a homopolymer with higher molecular weight than that by former method was obtained. Copolymers with M_n higher than 60000 could be obtained at 0–5 mol% of **3c** in copolymerization. Copolymerization with 10 mol% of **3c** was very slow and could not give similar M_n to the others. The composition of **3c** in the copolymers was approximately estimated from the methylene proton resonance intensities of CH₂(d) and (CH₂)₁₅(b) as shown in Figure 2. The compositions of **3c** in **PBS2(0.3)** and **PBS2(0.5)** were obscure because of the few peaks b.

Table V. Thermal properties of copolymers

Run	Copolymer	T_g (°C)	T_m (°C)	ΔH_m (mJ mg ⁻¹)	Td2
1	PBS2(0)	-35.9	116.1	108.1	309.3
2	PBS2(0.3)	-36.6	114.9	66.5	306.9
3	PBS2(0.5)	-38.0	113.7	93.4	300.7
4	PBS2(1)	-36.7	115.0	98.9	310.5
5	PBS2(2)	-36.6	113.7	88.3	310.6
6	PBS2(5)	-36.4	108.8	89.4	308.1
7	PBS2(10)	-18.8	105.2	94.3	307.6

The composition of **3c** in copolymer was similar to the feed composition of **3c** at 1 to 10 mol% **3c**.

Table V shows the thermal properties of obtained

Figure 2. ^1H NMR spectrum of **PBS2(5)**.**Table VI.** Tensile strength of copolymers

Run	Copolymer	Elastic MPa	Yield Stress MPa	Break Stress MPa	Break Strain %
1	PBS2(0)	239	27.2	35.5	370.2
2	PBS2(0.3)	216	23.1	56.3	720.7
3	PBS2(0.5)	225	24.8	51.5	709.5
4	PBS2(1)	260	22.3	50.0	730.7
5	PBS2(2)	180	20.5	50.9	777.0
6	PBS2(5)	147	17.2	40.5	833.4
7	PBS2(10)	131	13.8	13.7	16.4

copolymers. These properties were not so changed at 0 to 10 mol% of **3c**.

Table VI shows the tensile tests of copolymers. Homopolymer **PBS2(0)** shows greater break strain than **PBS1** because of high M_n of 69400. The elastic modulus and yield stress decreased, and break strain increased with **3c** in the copolymers. A copolymer thus becomes more flexible with **3c**. When 5 mol% of **3c** was included in a copolymer the break stress of the copolymer was 833%.

Biodegradation kinetics are important in biodegradable plastics. Figure 3 shows the biodegradation experimental results of **PBS2(0)**, **PBS2(1)**, and **PBS2(5)** film samples in commercial compost soil under 30 °C and 95% RH. Biodegradability was thus expressed as weight loss as a function of buried time for 25 × 25 mm film samples. Although the biodegradability of **PBS2(0)** and **PBS2(1)** was almost the same, weight loss of **PBS2(5)** was less than **PBS2(0)** and **PBS2(1)**. Although many copolymers are more biodegradable than the homopolymer for the low crystallinity,^{7,9} copolymer **PBS2(5)** was less biodegradable than the homopolymer **PBS2(0)**, possibly because of the hy-

Figure 3. Buried time dependence of biodegradation.

drophobic alkyl long chain of **3c**. Biodegradability control may be possible according to type and composition of **3**.

CONCLUSION

Poly(butylene succinate) copolymers including small amount of **3** had larger break strain than homopolymer.

Molecular weight decreased with increasing **3**, because the secondary alcohol of **3** was less reactive than the other primary alcohols, and could not be esterified nor copolymerization made progress. Only 1 mol% **3c** having an alkyl long chain decreased M_n of copolymer at 23000. The copolymer including 0.3% **3c** had the largest break strain. So a new synthetic method to accelerate copolymerization was designed so that diols of **3c** are first esterified by succinic anhydride and then copolymerization with 1,4-butanediol. M_n of copolymers at 0 to 5 mol% of **3c** were higher than 60000 using the new method. The elastic modulus and yield stress of copolymers decreased, and break strain increased with **3c** in copolymers. The copolymer thus becomes more flexible with increasing **3c**. At 5 mol% **3c** in the copolymer, break stress reached 833%.

Biodegradation tests of copolymers were carried out in commercial compost soil under 30 °C and 95% RH. Although the biodegradability of **PBS2(0)** and **PBS2(1)** was almost the same, the weight loss of **PBS2(5)** was less than **PBS2(0)** and **PBS2(1)**. The delay of biodegra-

dation by copolymerization with **3c** shows the possibility of biodegradability control by type and composition of **3**.

REFERENCES

1. S. Takenouchi, A. Takasu, Y. Inai, and T. Hirabayashi, *Polym. J.*, **33**, 746 (2001).
2. T. Hayashi, H. Kanai, and T. Hayashi, *Polym. J.*, **33**, 38 (2001).
3. J. Li, Y. He, and Y. Inoue, *Polym. J.*, **33**, 336 (2001).
4. H. Pranamuda, R. Chollakup, and Y. Tokiwa, *Appl. Env. Microbiology*, **65**, 4220 (1999).
5. Y. He, T. Masuda, A. Cao, N. Yoshie, Y. Doi, and Y. Inoue, *Polym. J.*, **31**, 184 (1999).
6. H. Pranamuda, Y. Tokiwa, and H. Tanaka, *Appl. Env. Microbiology*, **61**, 1828 (1995).
7. A. Cao, T. Okamura, C. Ishiguro, K. Nakayama, Y. Inoue, and T. Masuda, *Polymer*, **43**, 671 (2002).
8. Y. Taguchi, A. Oishi, K. Fujita, Y. Ikeda, K. Watanabe, and T. Masuda, *J. Oleo Sci.*, **49**, 825 (2000).
9. H. Shirahama, A. Kanetani, and H. Yasuda, *Polym. J.*, **32**, 280 (2000).