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Studies on syntheses and physical characterization of biodegradable aliphatic poly(butylene succinate-*co*-ε-caprolactone)s

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Abstract

Biodegradable aliphatic poly(butylene succinate-*co*-ε-caprolactone) (PBSCs) were synthesized through a polycondensation with titanium tetraisoproxide (TTP), diphenylphosphinic acid (DPPA) and stannous octoate ($Sn(Oct)_2$) as the novel co-catalysts. By means of gel permeation chromatography (GPC) and nuclear magnetic resonance spectrometer (NMR), it was revealed that the PBSC copolyesters had number average molecular weights M_n higher than 5.0×10^4, and that the polycondensations were in well agreement with a random copolymerization model. With respect to thermal properties, melting point, heat of fusion and glass transition temperature were found to decrease with increasing the CL/BS unit molar ratio up to 0.92, while thermal stability monotonously decreased with increasing the CL unit population spanning the whole CL unit composition. X-ray diffraction patterns indicated that the BS-rich/CL-rich PBSC organized the corresponding PBS/PCL-type of crystal structure. Moreover, it is worth to note that the PBS copolymerized with an appropriate amount of the minor CL component could significantly increase the fracture elongation of the resultant PBSC, and that mechanical properties of PBSC strongly depended on its CL unit population. In addition, biodegradabilities of PBSCs as well as PBS and PCL were tentatively assessed in a kind of compost soil, and the results suggest that chain flexibility may play an important role in the biodegradation as another factor besides the specificity of unit chemical structure and morphology.

Keywords: Biodegradable aliphatic PBSC; Polycondensation; Physical properties

1. Introduction

Recently, biodegradable polymers are of increasing interest and attracting much attention from material researchers and industry, owing to the increasing environmental concerns about waste pollution. It has been reported that they can be efficiently degraded into non-toxic water-soluble oligomers by a great number of microorganisms widely distributed in the environment, such as bacteria, fungi and so on, and then the water-soluble oligomers can be reutilized finally into energy and products of carbon dioxide and water through several metabolic procedures of microorganisms [1–4].

Aliphatic polyesters have been recognized as the environmental friendly biodegradable polymers. Up to date, syntheses of biodegradable aliphatic polyesters have been extensively studied. Polycondensation of a dicarboxylic acid and a diol as well as hydoxycarboxylic acid can produce high molecular weight aliphatic polyesters such as poly(ethylene succinate) (PES) [5–8], poly(butylene succinate) (PBS) [5,6,8–12], poly(butylene adipate) (PBA) [6], poly(glycolic acid) (PGA) [13], poly(lactic acid) (PLA) and so on [4,14]. Furthermore, in order to satisfy the variation in the physical property demanded for different application fields numerated as fiber, film, molds etc. a number of biodegradable aliphatic copolyesters have been successfully developed to regulate their chemophysical properties [5–6,8]. On the other hand, ring opening polymerization ROP of lactone, latide, lactum as well as

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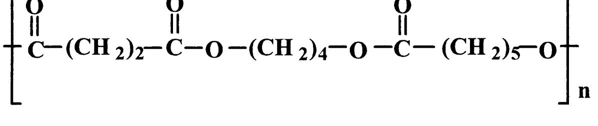
some cyclic compounds provided an alternative way to synthesize biodegradable aliphatic polyesters with several organometallic catalysts in solution or bulk, for instance, poly(β-propiolactone) (PPL), poly(β/γ-butyrolactone), poly(ε-caprolactone) (PCL), poly(lactide)s with respective stereo regularities of the corresponding repeating units, poly(ε-caprolactum) etc. [14–17].

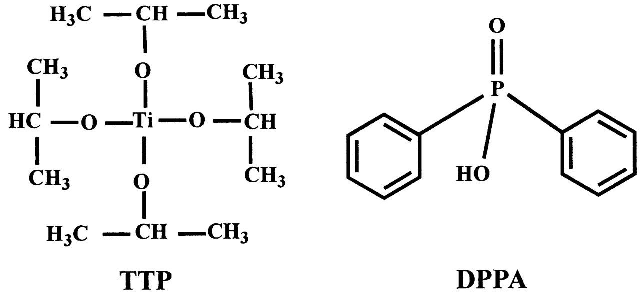
So far, poly(butylene succinate) (PBS) has been known as the biodegradable polyester. Since the pioneering work of Carothers et al. 70 years ago [18], it has been revealed considerably difficult to synthesize an aliphatic polyester bearing molecular weight high enough for the practical application. In the past decade, as an active response to the environmental concerns about the deposal of non-degradable municipal and industrial plastic waste, Showa high polymer Co. Ltd successfully developed high molecular weight commercial aliphatic PBS and a series of its copolyesters like poly(butylene succinate-*co*-butylene adipate) etc. [6,19]. It was reported that the diisocyanate was thereby applied as the chain-coupling agent to increase the molecular weight of the synthesized aliphatic polyesters. Now, high molecular weight PBS is expected as a feasible biodegradable polymer for the applications in the packaging, agricultural and medical fields etc. On the other hand, poly(ε-caprolactone) is another well studied biodegradable aliphatic polyester which can be easily synthesized through a ring opening polymerization of ε-caprolactone in the presence of Al, Sn, Ti or other organometallic catalysts [20–23]. Semi-crystalline PCL was reported to be degraded by extracellular depolymerase or in various environments such as soil, river water, marine and so forth, however, a relatively low melting point of about 64°C practically limited the field of application [24].

This paper will present the polycondensation results of aliphatic copolyester PBSCs in the presence of our original co-catalysts of titanium tetraisoproxide, diphenylphosphinic acid and stannous octoate in bulk (Schemes 1 and 2) (Chemical structure of PBSC, Chemical structures of TTP and DPPA) [25]. Furthermore, the ε-caprolactone repeating unit composition dependencies of thermal and crystallization behaviors and mechanical properties of the prepared PBSCs were studied. With the aid of X-ray diffractometer, their crystalline structures were simultaneously investigated. In addition, biodegradabilities of the prepared copolyester film samples were assessed in a commercial compost soil under 30°C and 95% relative humidity (RH). As a result, the correlation between the polymer structure and biodegradation behavior will thus be carefully discussed.



$$\left[\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-(CH_2)_5-O \right]_n$$

Scheme 1.



Scheme 2.

2. Experimental

2.1. Materials

Succinic acid (SA), 1,4-butanediol (BD), titanium tetraisoproxide (TTP) and stannous octoate ($Sn(Oct)_2$) (Wako pure chemical) were used without further purification. Diphenylphosphinic acid (DPPA) was also used as purchased from Aldrich chemical. ε-caprolactone (ε-CL) from Wako pure chemical was dried with CaH_2 over night, and then distilled under the reduced pressure less than 1.0 mm Hg prior to the synthesis. In addition, the commercial soil for biodegradation test was originated from the composted yard soil collected at Tsukuba, Japan.

2.2. Syntheses of poly(butylene succinate-co-ε-caprolactone)s

A three-necked 200 ml flask was charged with 0.500 mol of succinic acid, 0.525 mol of 1,4-butanediol and the predetermined amount of ε-caprolactone under a dry N_2 atmosphere. Further, 0.330 mmol of titanium tetraisoproxide, 0.165 mmol of diphenylphosphinic acid DPPA and $Sn(Oct)_2$ with the $Sn(Oct)_2$/ε-CL molar ratio equal to 0.1% were added under the gentle agitation. The flask assembled with a gas introduction inlet and an outlet connected with a condenser was firstly immersed in a silicon oil bath preset at 230°C, and heated to remove the esterification reaction byproduct of water for 1 h. Subsequently, the condenser was removed, and polycondensation was carried out under the gradually reduced pressure with a final degree of vacuum less than 0.5 mm Hg. The polycondensation of PBSC was ended when the real-time torque of the mechanical stirrer (220 rpm) approached a maximum value, which was simultaneously monitored through an attached torque sensor (Keyence Co. Ltd, Japan). Moreover, the as-prepared polyesters were further kept at ambient temperature for more than four weeks to prompt their crystallization to approach the equilibrium state prior to the characterization.

2.3. Analytical procedures

Measurements of ^1H and ^{13}C NMR spectra were conducted in $CDCl_3$ solution under ambient temperature

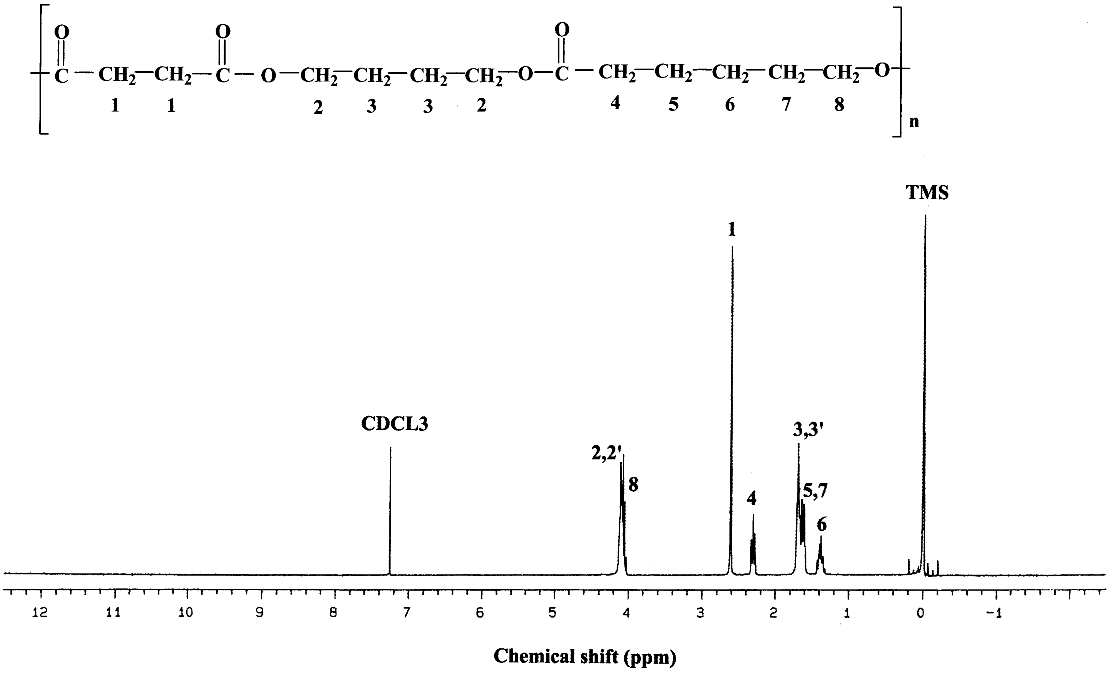


Fig. 1. 300.08 MHz ^{1}H NMR spectrum of poly(butylene succinate-*co*-ε-caprolactone) bearing the CL/BS molar ratio of 0.92.

on a Varian 300BB FT-NMR spectrometer operated at 300.08 and 75.46 MHz, respectively. Accordingly, the composition of ε-caprolactone repeating unit involved in the poly(butylene succinate-*co*-ε-caprolactone) was approximately estimated from the methylene proton resonance intensities of $CH_2(1)$ and $CH_2(4)$ as shown in Fig. 1. In addition, their sequence distribution of the BS and CL repeating units was also investigated on the basis of ^{13}C NMR signals of the methylene $CH_2(3,3')$ and $CH_2(10,10')$ as shown in Fig. 2.

Molecular weights of the prepared PBSC copolyesters were measured by a Toso Hlc 8020 gel permeation chromatography (GPC) equipped with a UV and a refractive index RI detector. A set of Toso Tsk-gel GMH_{XL}-L, $G2000H_{XL}$ and $G1000H_{XL}$ columns were hereby applied with $CHCL_3$ as the eluant at a flowing rate of 1.0 ml/min under 40°C.

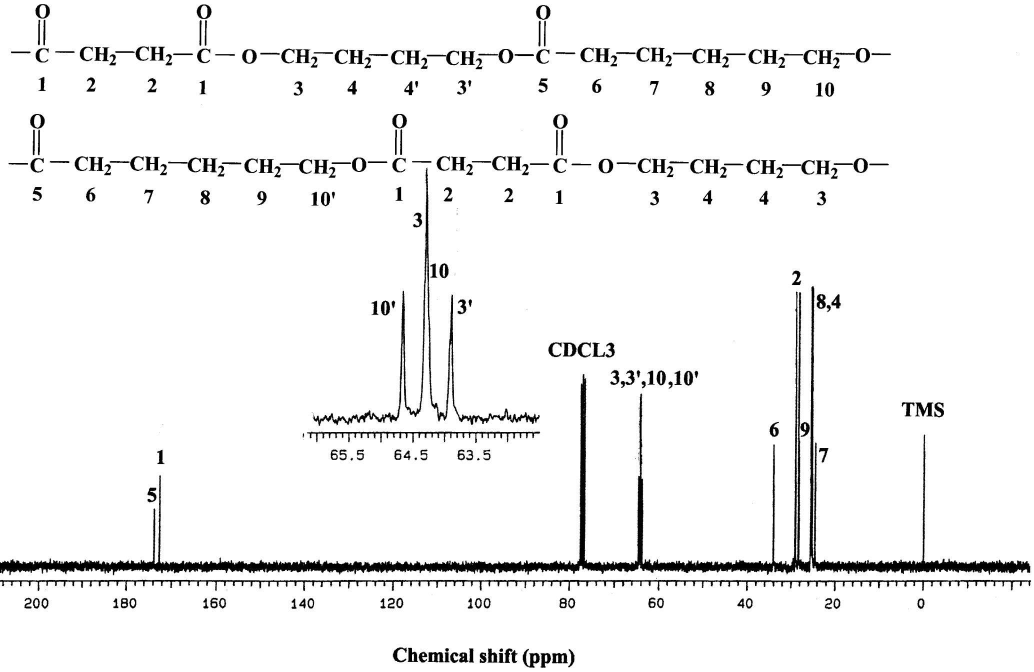


Fig. 2. 75.46 MHz ^{13}C NMR spectrum of poly(butylene succinate-*co*-ε-caprolactone) bearing the CL/BS molar ratio of 0.92.

Table 1
Syntheses of poly(butylene succinate-*co*-ε-caprolactone)

Number	Feed molar ratio ε-CL/SA/BD	Reaction time (h)[a]	CL/BS molar ratio in copolymers[b]	Molecular weight[c]		
				$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
1[d]	0:1.00:1.05	4.3	0	6.19	10.21	1.65
2[d]	0.10:1.00:1.05	2.9	0.08	5.71	9.85	1.73
3[d]	0.20:1.00:1.05	3.7	0.18	5.62	9.68	1.72
4[d]	0.50:1.00:1.05	3.8	0.46	5.55	9.37	1.69
5[d]	1.00:1.00:1.05	3.8	0.92	5.35	8.71	1.63
6[d]	5.00:1.00:1.05	2.8	4.52	5.10	8.02	1.57
7[e]	1.00:0:0	1.3	–	4.35	6.64	1.53

[a] Polycondensation time.
[b] The CL/BS molar ratios were evaluated by ^{1}H NMR.
[c] Molecular weight was measured by a Toso 8020 GPC.
[d] PBSCs were synthesized with 0.330 mmol TTP, 0.165 mmol DPPA and $Sn(Oct)_2$ with $Sn(Oct)_2$/ε-CL molar ratio equal to 0.1% as co-catalysts under 230°C.
[e] PCL sample was synthesized at 200°C with stannous octoate as the catalyst.

Polystyrene standards with narrow molecular weight distribution were employed to generate a calibration curve. Thus, M_n, M_w and polydispersity index M_w/M_n were estimated for the investigated polyesters through a Toso Sc-8020 controller.

Thermal analyses were carried out on a Seiko DSC Ssc-5200 and a TG/DTA SSC-5200H. Each samples (about 10 mg) prepared as aforementioned was pre-sealed in a aluminum pan, and then DSC thermal diagram was recorded at a heating speed of 10°C/min from −80 to 200°C (the first heating scan). After a rapid quenching, the polyester sample was reheated from −100 to 200°C at a heating rate of 20°C/min (the second heating scan). Melting point T_m was taken as the main peak top of the endothermic curve, and heat of fusion ΔH_m was estimated as the integrals of the endothermic curves. Cold crystallization temperature T_{cc} and glass transition temperature T_g were evaluated as the crystallization peak top and the midpoint of heat capacity change C_p of the exothermic curve (the second DSC trace), respectively. As to thermal stability, the prepared polyester sample (about 10.0 mg) was heated from 50 to 500°C at a scanning rate of 10°C/min under an inert atmosphere of N_2, TG/DTA traces were thus recorded and analyzed. A temperature $T_d(-2\ \text{wt\%})$, at which 2.0 wt% of the original polyester sample has already been thermally degraded and lost, was hereby taken as an index to express its thermal stability.

Wide-angle X-ray diffraction patterns were recorded on a Rigaku-200 X-ray diffraction instrument (50 kV/180 mA) for the semi crystalline polyester samples. The nickel-filtered Cu Kα X-ray beams with a pinhole graphite monochromator were applied as the source ($\lambda = 0.154$ nm).

Mechanical properties of the PBSC film samples were measured under 25°C on a Toyo Baldwin Tensilon SS-207-EP instrument according to JIS K-7113. PBSC film samples with the dimensions of 25 mm × 5 mm × 0.25 mm were prepared with a hot-press plate, and then kept at ambient temperature for more than one month before the measurements. The stress was recorded as a function of strain at a universal crosshead drawing speed of 10.0 mm/min, and mechanical properties of PBSC samples were thus estimated.

Assessment of biodegradability was tentatively implemented under 30°C and 95% RH in a kind of compost soil collected in Tsukuba, Japan. PBSC film samples (25 mm × 25 mm, thickness: 0.25 mm) prepared as aforementioned were buried, and sampled periodically every week. After washing with the distilled water three times and then drying in vacuo, an averaged weight loss of three film samples ($W_0 - W_t$) was used to express its biodegradability in soil, where W_0, W_t denote the original weight and that sampled at *t* week, respectively.

3. Results and discussion

3.1. Polycondensation of poly(butylene succinate-co-ε-caprolactone)s

Table 1 summarizes the polycondensation results of poly(butylene succinate-*co*-ε-caprolactone)s in the presence of titanium tetraisoproxide (TTP), diphenyl-phosphinic acid (DPPA) and $Sn(Oct)_2$ as the co-catalysts under 230°C. As for the PCL homopolymer, it was synthesized under 200°C with $Sn(Oct)_2$ as the initiator of the ring opening polymerization. In a view of Table 1, aliphatic PBSCs with M_n higher than 5.0×10^4 were synthesized within a short polycondensation time scale of 2–4 h, regardless of their different CL/BS unit molar ratios. Since the research of Carothers [18], it has been well known that the generation of tetrahydrofuran THF and the volatile oligomer esters as the polycondensation byproducts through a depolymerization reaction was found to limit a further increase in the degree of polymerization for the aliphatic polyester. In our previous research [25], the co-catalysts of TTP and DPPA have been revealed to be effective to suppress the side reaction of generating THF and the volatile oligomer esters and decrease the viscosity of the reaction mixture, furthermore, the synthesized aliphatic polyester PBS was found to show much larger elongation than those ever reported. With regard to PBSC synthesis, 1,4-butanediol/succinic acid feeding molar ratio was fixed to 1.05, while ε-caprolactone/succinic acid was varied from 0.10 to 5.00 for preparing PBSCs bearing different ε-caprolactone unit populations, respectively. Furthermore, besides the catalysts of TTP and DPPA (TTP/succinic acid molar ratio = 0.66‰, DPPA/TTP molar ratio = 0.50), a third catalyst of $Sn(Oct)_2$ was also added with a fixed $Sn(Oct)_2$/ε-caprolactone monomer ratio equal to 0.1 mol%. Fig. 1 shows the ^{1}H NMR spectrum of the PBSC copolyester, and the proton resonance signals of the PBSC copolyester were accordingly assigned to those originated from the respective methylene protons as indicated in Fig. 1 [9,22]. Thus, the molar ratios of the CL repeating unit to butylene succinate (BS) were estimated on the basis of the corresponding resonance intensities of $CH_2(1)$ [BS unit] and $CH_2(4)$ [CL unit], and the results are shown in Table 1. The higher ε-CL/SA molar ratio is in the feeding reaction mixture; the higher molar composition of CL repeating unit can be seen for the PBSC copolyester. The relatively lower CL/SA molar ratios in the resultant PBSCs than those of the feeding ε-CL/SA maybe stem from the evaporation of a few amount of ε-CL monomer during the esterification reaction under 230°C.

Fig. 2 presents the 75.46 MHz ^{13}C NMR spectrum of the PBSC copolyester with the CL/BS molar ratio equal to 0.92. The splits of ^{13}C resonance signal illustrated as an inset in Fig. 2 were reasonably assigned to 3, 3′, 10, 10′ originated from the sequence distributions of BS and CL repeating units, i.e. $S^*C(10')$ (64.67 ppm), $S^*B(3)$ (64.30 ppm), $C^*C(10)$ (64.26), $B^*C(3')$ (63.89 ppm), where S, B and C denote the respective succinic acid, 1,4-butanediol and ε-caprolactone moieties involved in the copolyester chain. Theoretically, if the polycondensation reaction is strictly in accordance with the random statistical polymerization model, the split intensity ratio of $I_{10'}(S^*C)/[I_3(S^*B) + I_{10}(C^*C)]/I_{3'}(B^*C)$ will be equal to $(2[S]^*[C])/(2[S]^*2[B] + [C]^*[C])/(2[B]^*[C])$, where [S], [B], [C] indicate the molar compositions of the aforementioned corresponding moieties. In the case of PBSC (CL/BS = 0.92), the theoretical $I_{10'}(S^*C):[I_3(S^*B) + I_{10}(C^*C)]:I_{3'}(B^*C)$ were calculated to be 0.38:1.00:0.38. In contrast, the result experimentally estimated by ^{13}C NMR is about 0.36:1.00:0.37, indicating that the polycondensation in this study is in well agreement with the random copolymerization model.

3.2. Thermal properties

In this study, thermal properties were characterized by means of DSC and TG/DTA for the PBSC copolyesters as well as homopolymer PBS and PCL. Figs. 3 and 4 illustrate the DSC thermal diagrams as a function of CL/BS molar ratio measured by the first and second DSC heating scans.

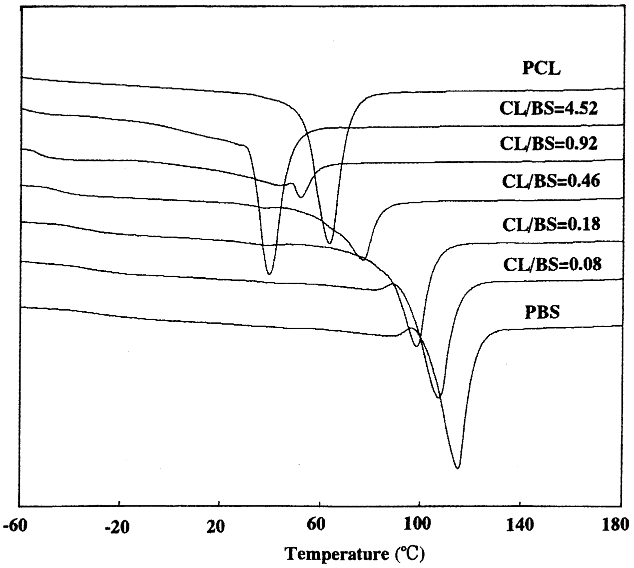


Fig. 3. DSC thermal diagrams of the PBSC copolyesters as well as PBS and PCL by the first heating scan.

With respect to homopolymer PBS and PCL, melting point T_ms of about 117 and 64°C are exhibited, respectively, while the melting peak of the PBSC copolyester shifts toward a relatively lower temperature with an increase in the CL/BS molar ratio up to 4.52. Moreover, DSC traces illustrated in Fig. 4 depict that the glass transition of the PBSC copolyester monotonously moves toward a lower temperature when the CL/BS unit molar ratio is increased. This result implies that the higher CL/BS molar ratio of PBSC copolyester is, the higher chain/segmental mobility will be revealed, and that the PBS copolymerized with the CL unit could enhance the chain/segmental mobility inside

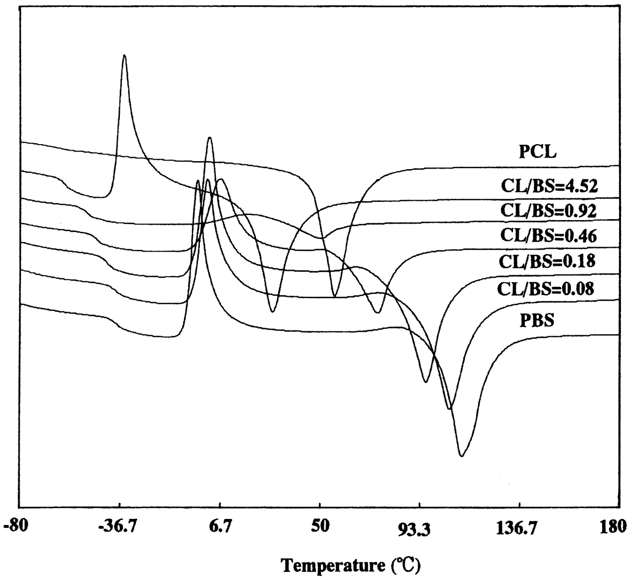


Fig. 4. DSC thermal diagrams of the PBSC copolyesters as well as PBS and PCL by the second heating scan.

Table 2
Thermal properties of poly(butylene succinate-*co*-ε-caprolactone)

Number	Sample code	T_{m}[a] (°C)	ΔH_{m}[a] (J/kg)	T_{g}[b] (°C)	T_{cc}[b] (°C)	T_{d} (−2 wt%)[c] (°C)
1	PBS	116.7	87.1	−36.3	−2.9	329.6
2	CL/BS = 0.08	107.3	77.4	−38.7	1.0	311.4
3	CL/BS = 0.18	98.2	71.9	−42.0	1.9	308.8
4	CL/BS = 0.46	76.4	62.9	−45.7	6.2	291.3
5	CL/BS = 0.92	51.7	50.9	−50.9	17.8	291.1
6	CL/BS = 4.52	39.2	81.1	−58.7	−34.9	268.7
7	PCL	63.6	109.8	−62.4	n.d.[d]	267.7

[a] T_{m} and ΔH_{m} were measured by the first DSC scan at a heating rate of 10°C/min.

[b] T_{g} and T_{cc} (cold crystallization temperature) were estimated from the second DSC heating traces at 20°C/min after a rapid quenching.

[c] $T_{\mathrm{d}}(-2\ \mathrm{wt}\%)$ was measured by TG/DTA with a scanning rate of 10°C/min.

[d] Not detected.

the amorphous region for the PBSC copolyesters. In general, the resultant thermal properties of melting point T_{m}, heat of fusion ΔH_{m}, glass transition temperature T_{g} and cold crystallization temperature T_{cc} are summarized in Table 2. It is seen that an incorporation of the CL structural moiety into the PBS polyester chain considerably retarded the crystallizability for the PBSC copolyester. As a result, their apparent heat of fusions decreased as compared with that of PBS, indicating a decrease in the crystallinity.

In addition, thermal stability is also well known as an important factor for the polyesters, which will limit their practical application [26]. Fig. 5 presents the thermal gravimetrical TG traces as a function of the CL/BS unit molar ratio, from which −2.0 wt% thermal degradation temperatures $T_{\mathrm{d}}(-2.0\ \mathrm{wt}\%)$ as defined in Section 2 were accordingly estimated and summarized in Table 2. PBS was found to exhibit a $T_{\mathrm{d}}(-2.0\ \mathrm{wt}\%)$ of about 330°C considerably higher than that of PCL, and $T_{\mathrm{d}}(-2.0\ \mathrm{wt}\%)$ approximately decreased monotonously along with an increase in the CL unit population in the copolyester. Hence, it can be concluded that PCL copolymerized with the BS repeating unit can increase its thermal stability.

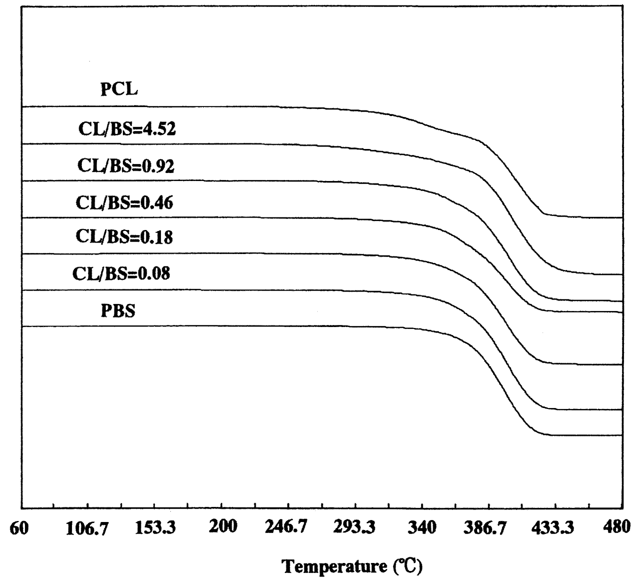


Fig. 5. TG traces of the PBSC copolyesters as well as PBS and PCL.

3.3. X-ray diffraction and crystal structure

With respect to crystal structure, poly(butylene succinate) has been extensively studied and reported to organize a monoclinic crystal structure with the lattice parameters as $a = 0.523$ nm, $b = 0.908$ nm, $c = 1.079$ nm and $\beta = 123.87°$ [11,12]. In this study, Fig. 6 shows the wide angle X-ray diffraction WAXD patterns of semi-crystalline PBS, PCL as well as the PBSC copolyesters with various CL/BS molar ratios. It is revealed that the PBSC copolyesters with the CL/BS molar ratios from 0.08 to 0.92 depict the same diffraction pattern as that of PBS, implying that they did organize the same crystal packing structures. In contrast, the sample of PBSC–CL/BS = 4.52 is revealed to form the PCL-type of high order crystal structure.

3.4. Mechanical properties

Mechanical properties were measured at a drawing rate of 10 mm/min for the semi-crystalline PBSC film samples as well as homopolymer PBS and PCL. According to Fig. 7, the mechanical properties were thus estimated as an averaged value of three samples for each polyester or copolyester, and the results are summarized in Table 3. It is revealed that the results of elasticity of modulus, yield stress and fracture stress tend to decrease with increasing the molar population of the CL or BS unit when the corresponding CL or BS appears as the minor component involved in the PBSC copolyester. This can be readily accounted for the decrease in the crystallinity as discussed on the basis of ΔH_{m} data. Furthermore, it is worth to note that to polymerize PBS with a few amount of CL unit could significantly modify the fracture elongation behavior without a remarkable loss in its mechanical strength for the PBSC–CL/BS = 0.08. Moreover, the PBSC copolyester samples (nos. 5 and 6) as depicted in Table 3 show rubber-like feature with much larger fracture elongation and low mechanical strength.

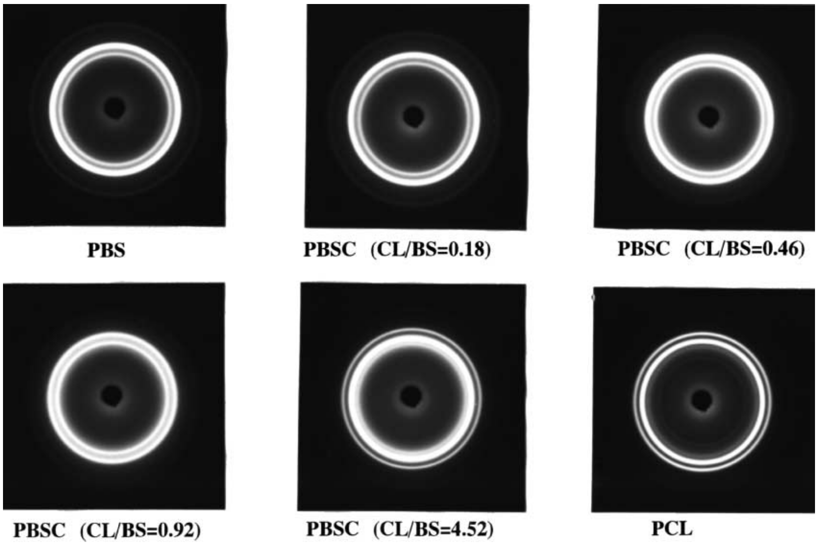


Fig. 6. The wide-angle X-ray diffraction patterns of the PBSCs as well as PBS and PCL.

3.5. Biodegradation of film samples in the compost soil

Biodegradable poly(butylene succinate) as well as its copolyesters has been reported to be subject to enzymatic attack, [10,27] and also be able to degrade by various environmental microorganisms such as bacteria, fungi and actinmycetes [9,24]. On the other hand, poly(ε-caprolactone) has also been known as a biodegradable polymer which can be degraded by the lipases with various origins and microorganisms of PCL-degrader [24,28,29]. With regard to the biodegradation mechanism, it has been revealed that the biodegradation follows a continuous two-step reaction model, i.e. the enzyme excreted by PBS or PCL degrader is firstly adsorbed on the surface of film, and then scissor the ester bonds of polyester chains [30]. In the case of a biodegradable copolyester or a binary biodegradable blend, a component was be found to be able to induce the biodegradation of the partner, e.g. for the bacteria poly(3-hydroxybutyric acid-*co*-3-hydroxypropionic acid) (P(3HB-*co*-3HP)) or the binary poly(3-hydroxy-butyric acid) (P(3HB))/chemosynthetic poly(β-propiolactone) (P(3HP)) blend, 3HB comonomer or P(3HB) blend component was reported to be able to induce the biodegradation of 3HP comonomer or the P(3HP) blend partner in a natural river water [31].

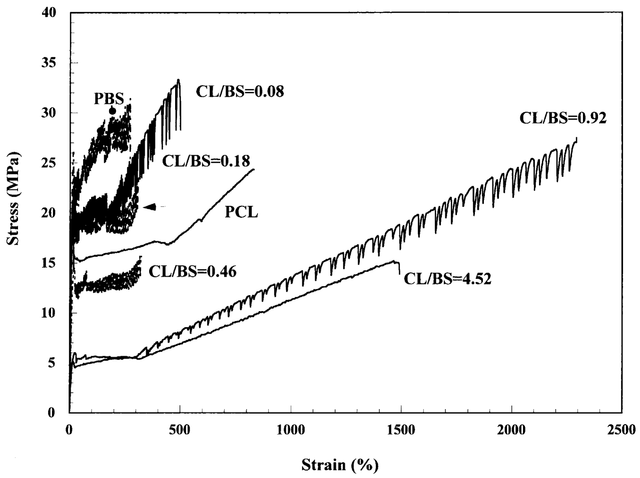


Fig. 7. Mechanical properties of PBS, PCL and the PBSCs at a drawing rate of 10 mm/min.

Fig. 8 presents the biodegradation experimental results of the PBSC copolyesters, PBS and PCL film samples in a commercial compost soil under 30°C and 95% RH. The biodegradability was hereby expressed in a term of weight loss as a function of the buried time for the $25 \times 25\ \mathrm{mm}^2$ film samples. It is confirmed that each copolyester or homopolymer was degraded in this kind of compost yard soil, and that the PBSC copolyesters exhibited degradabilities considerably higher than those of PBS and PCL. In particular, the PBSC sample with the CL/BS unit molar ratio equal to 4.52 exhibited fast biodegradation rate and the highest biodegradability, even though its crystallinity is higher than that of the PBSC sample with the CL/BS unit molar ratio equal to 0.92. This phenomenon may be accounted for an total effect of morphology and the chain/segmental flexibility inside the amorphous regions, that is, the higher chain flexibility and the lower crystallinity are for the PBSC copolyester, the higher degradability will be revealed. Therefore, besides the specificity of the unit chemical structure and crystallinity, the chain/segmental flexibility as another factor is suggested to play an important role in the biodegradation behavior for the aliphatic PBSC copolyesters.

4. Conclusions

In summary, biodegradable aliphatic copolyester PBSCs

Table 3
Mechanical properties of poly(butylene succinate-*co*-ε-caprolactone)s (sample dimensions: 25 mm × 5 mm × 0.25 mm)

Number	Sample code	Modulus of elasticity (MPa)	Yield stress (MPa)	Fracture stress (MPa)	Fracture strain (%)
1	PBS	286	26.5	28.8	278
2	CL/BS = 0.08	272	20.5	26.5	498
3	CL/BS = 0.18	234	19.3	20.8	290
4	CL/BS = 0.46	128	11.2	13.4	313
5	CL/BS = 0.92	38	2.3	23.2	2246
6	CL/BS = 4.52	104	3.95	14.4	1391
7	PCL	321	18.7	23.2	822

were derived from 1,4-butanediol, succinic acid and ε-caprolactone through the polycondensation with TTP, DPPA and $Sn(Oct)_2$ as the co-catalysts. GPC results revealed that PBSC copolyesters as well as PBS bearing number average molecular higher than 5.0×10^4 were efficiently synthesized within a short polycondensation time scale of 2–4 h, regardless of their different CL/BS unit molar ratios. And the sequence distributions analyzed by means of ^{13}C NMR demonstrated that the polycondensations of the PBSCs were in well accordance with the random copolymerization model. Moreover, the thermal properties characterized by DSC and TG/DTA indicated that an incorporation of the minor structural moiety of CL or BS significantly retarded the chain crystallizability of the PBSC copolyester, and a monotonous decrease in the glass transition temperature and the thermal stability was observed with increasing the CL unit population in the PBSC copolyester. Furthermore, WAXD experimental result demonstrated that the BS-rich/CL-rich copolyesters organized the corresponding PBS-type/PCL-type crystal packing structures. As for mechanical properties, the extremely high fracture elongations were revealed for copolyesters, and the PBSC samples bearing the respective CL/BS unit molar ratios equal to 0.92 and 4.52 exhibited the rubber-like features with much larger elongation. Moreover, results of biodegradation in the compost soil demonstrated the biodegradability of both homopolymers and the PBSC copolyesters, and the chain flexibility is suggested as another factor to play an important role in the PBSC biodegradation besides the specificity of the unit chemical structure and morphology.

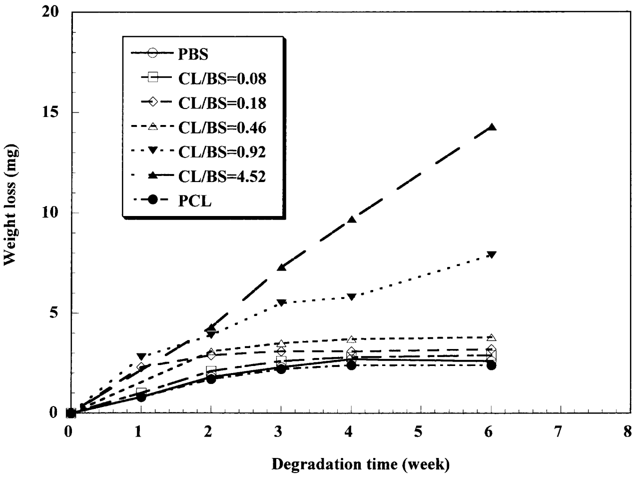


Fig. 8. The buried time dependence of biodegradation of PBS, PCL and the PBSC film samples in the compost soil.

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