



# Improving the marine biodegradability of poly(alkylene succinate)-based copolymers

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## Abstract

We report the syntheses of novel marine biodegradable poly(ethylene succinate) (PES)- and poly(butylene succinate) (PBS)-based copolymers containing different dicarboxylic acid (DCA) units with various carbon numbers and different feed ratios. Biochemical oxygen demand tests demonstrated that some of the obtained PES- and PBS-based copolymers were biodegradable in seawater. Specifically, polymers with longer-chain DCA units, even at low contents, exhibited marine biodegradability. The thermomechanical properties of the copolymers, such as their thermal stabilities, melting points, glass transition temperatures, tensile moduli, strains at break, and stresses at break, also varied with the DCA contents. These results indicated that the thermomechanical properties and the marine biodegradabilities of the PES- and PBS-based copolymers were regulated by controlling their structures and DCA contents. The polymers obtained in this study may replace general-purpose polymers. Our approach may also be applicable to other polymeric materials. Furthermore, our findings pave the way for the rational design and preparation of polymeric materials that are biodegradable in environments other than oceans and have good thermomechanical properties.

## Introduction

Plastics are used in various applications and are essential materials in daily life owing to their light weights, durabilities, and workabilities. Large amounts of plastic materials are produced annually. For instance, in 2015, 322 million tons of plastics were produced, and most of them

were used in packaging applications [1, 2]. Unfortunately, given the global increase in plastic production, the amount of mismanaged plastic waste released into the environment has increased drastically, and much of this waste is discarded directly into oceans and rivers. A report in 2010 stated that the amount of annual plastic waste discarded into the ocean totaled 4.8–12.7 million tons [3]. Because plastic waste exhibits poor biodegradability in both freshwater and seawater, its presence in waterways can cause various and widespread problems in the environment, natural habitats, and even the food supply chain. For example, microplastics generated from discarded plastic wastes, along with the toxic substances bound to them, can harm the health of humans and other living things [4, 5]. Discarded plastic fishing equipment such as fishing nets and ropes can lead to the deaths of marine creatures owing to accidental ingestion and entanglement [6]. Therefore, marine pollution caused by plastic waste has become a major social problem that must be addressed.

Unfortunately, some types of plastic wastes, such as microfibers generated by washing synthetic clothing or fishing gear that is accidentally lost, are difficult to collect and control. Thus, marine biodegradable polymers have attracted significant attention [7, 8]. Biodegradation

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generally refers to the process of degrading polymers to carbon dioxide and water, some of which can then be used for biomass formation by microorganisms [9]. According to the technical standards for biodegradability in marine environments issued by regulatory bodies such as the International Organization for Standardization, the ASTM International, and the Organisation for Economic Co-operation and Development, polymers must generally biodegrade within 60 d, and their maximum full-degradation period must not exceed two years for them to be certified as biodegradable [10].

For example, cellulose, which is the main component of plant cell walls, is widely known to be marine biodegradable and has been used in various applications [11]. Kasuya et al. evaluated the biodegradabilities of aliphatic polyesters prepared with both biosynthetic and chemosynthetic methods in different natural waters and reported that poly(hydroxyalkanoate) and poly(caprolactone) were biodegradable in seawater [12]. Tachibana et al. reported that nylon 4 (polyamide 4) synthesized via ring-opening polymerization of 2-pyrrolidone was biodegraded in seawater, although polyamides such as nylon 6 and nylon 66 are generally not biodegradable [13]. While there have been reported examples of marine biodegradable polymers, such as those described above, the variety of these polymers remains limited [14]. Thus, expanding the variety of marine biodegradable polymers and improving their properties are necessary to promote proper application and enable the replacement of existing nonbiodegradable polymers. However, only a few examples of marine biodegradable polymers have been developed as practical materials, and the narrow range available remains a crucial problem.

Polymers show poorer biodegradability in seawater than in other natural environmental waters because there are fewer microorganisms in seawater [15, 16]. However, some polymers are biodegraded in environments other than the ocean and have good physical properties. For example, poly(ethylene succinate) (PES), which is produced by polycondensation of succinic acid (SA) and ethylene glycol (EG), biodegrades easily in soil and river water within a month and has excellent gas-barrier properties [12, 17–25]. Poly(butylene succinate) (PBS), which is produced by the polycondensation of SA and 1,4-butanediol (BD), has good mechanical properties and is used in applications such as mulch film, disposable bags, and nonwoven fabrics [26, 27]. However, this polymer is less biodegradable than PES; for example, Doi et al. reported that PBS was not biodegraded in river water after a month [23]. The thermomechanical properties of these polymers can be adjusted via copolymerization with other monomers [28–32]. If the biodegradability of PES and PBS can be improved, new polymers with superior thermomechanical properties and marine biodegradability can be developed. Liu et al.

improved the degradation behavior of PBS-copolymers in seawater by incorporating lactic acid units and stated that facile hydrolysis of the polymer was important [33]; in this study, the degradation tests were conducted over a period of more than one year. Other examples in which similar enhancements of degradation were achieved by introducing a third monomer, such as glycolic acid or 6-hydroxyhexanoic acid, have been reported [34, 35]. In a study on the marine biodegradabilities of polymers with structures similar to those of PES and PBS, poly(ethylene adipate) synthesized via polycondensation of adipic acid (AdA), which is a dicarboxylic acid (DCA) with chains longer than those of SA and EG, was found to biodegrade in seawater within a month [12]. Based on these results, we hypothesized that long-chain DCA units were important for improving the biodegradability of these types of polymers [36, 37].

In this study, we investigated the syntheses, characterization, and marine biodegradation of PES- and PBS-based copolymers containing long-chain DCA units to develop novel marine biodegradable polymers. PES-based copolymers were obtained via copolymerization with DCAs containing different numbers of carbon (6, 8, 10, and 12) at DCA/(SA + DCA) feed ratios of 20, 15, 10, and 5 mol%, respectively, and the effect of the carbon content on the marine biodegradabilities of the obtained polymers was investigated. PES-based copolymers containing DCA units with over eight carbon atoms exhibited marine biodegradability. In addition, with more carbon atoms in the DCA units, the biodegradability of the copolymer in seawater is enhanced. Because the biodegradability of PBS is lower than that of PES, PBS-based copolymers were synthesized via copolymerization with various DCAs at a DCA/(SA + DCA) feed ratio of 20 mol% to enhance the biodegradability. PBS-based copolymers containing DCA units with over 10 carbon atoms exhibited marine biodegradability, and the effect of carbon number on these copolymers was identical to that observed with the PES-based copolymers. Furthermore, thermal analyses and tensile tests were conducted to confirm the effects of copolymerization and determine the most fundamental thermal and mechanical properties.

## Experimental section

The copolymers were synthesized via esterification and polycondensation and then characterized as follows:  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy were performed with a JEOL nuclear magnetic resonance (NMR) spectrometer (JNM-ECZ500). Size-exclusion chromatography (SEC) was performed with a Shimadzu gel permeation chromatography (GPC) system equipped with an

RID-20A refractive index detector, a Shodex GPC K-802 column, and a Shodex GPC K-806M column. Thermogravimetric analyses (TGA) were performed with an SII Nano Technology TG/DTA7200 thermal analyzer. Differential scanning calorimetry (DSC) measurements were performed with a PerkinElmer DSC8500 calorimeter. Biochemical oxygen demand (BOD) experiments were performed with a WTW OxiTop IDS BOD measurement system (Xylem, Inc.) under aerobic conditions in an incubator (LTE510, TOKYO RIKAKIKAI Co., Ltd.). Tensile tests were performed with a Shimadzu AG-50kNXDplus tensile tester. Moreover, a water contact angle (WCA) assay was performed with a Kyowa Interface Science contact angle meter (DMe-211), and X-ray diffraction (XRD) measurements were conducted with a Rigaku Nano-Viewer PILATUS 100 K unit.

## Materials

SA, suberic acid (SubA), sebacic acid (SebA), dodecanedioic acid (DDDA), titanium (IV) isopropoxide (TTIP), BD, AdA, chloroform ( $\text{CHCl}_3$ ), methanol, EG, chloroform- $d_1$  ( $\text{CDCl}_3$ ), and chromatography-grade  $\text{CHCl}_3$  were used for the syntheses and characterization procedures. All reagents and solvents were used as received without further purification.

## Copolymer synthesis

All copolymers were synthesized with a two-step melt polycondensation (esterification and polycondensation) protocol. SA (60 mmol, 7.1 g), DCA, and a diol (EG or BD) were added at an (SA + DCA):diol molar ratio of 1:1.05 to a three-necked separable glass flask equipped with a stirring device and vent. The flask was deoxygenated with a nitrogen flow and heated first at 200 °C for 1 h and then at 230 °C for 1 h. Subsequently, the system pressure was reduced to <0.5 kPa, and the flask was heated for 1 h. After esterification, a solution of TTIP ( $5 \times 10^{-3}$  mol% of the total molar amount of (SA + DCA)) in toluene was added to the mixture, and polycondensation was carried out at 230 °C and <0.5 kPa for 5 h. The resulting polyester was purified via dissolution in  $\text{CHCl}_3$  and precipitation with methanol. The polymer was dried overnight at 40 °C under vacuum. PES and PBS were also synthesized in the same manner without DCAs.

## Measurements

### NMR spectroscopy

$^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were performed at room temperature (approximately 25 °C) with an NMR

spectrometer operated at 500 and 125 MHz, respectively. The samples were dissolved in  $\text{CDCl}_3$ , and the spectra were referenced to tetramethylsilane (TMS,  $\delta$  0.00) and were analyzed with Mnova NMR software.

### Calculation of the DCA/(SA + DCA) content molar ratios in the copolymers

The DCA/(SA + DCA) content molar ratios in the copolymers were calculated from the integrated intensities of the signals from the  $\alpha$ -protons of the SA and DCA units, which appeared at approximately 2.6 and 2.3 ppm, respectively. The following formula was used:

$$\text{DCA}/(\text{SA} + \text{DCA}) \text{ content molar ratio} = I_{\text{DCA}}/(I_{\text{SA}} + I_{\text{DCA}}),$$

where  $I_{\text{SA}}$  and  $I_{\text{DCA}}$  are the integrated intensities of the signals for the  $\alpha$ -protons of the SA and DCA units, respectively.

### SEC

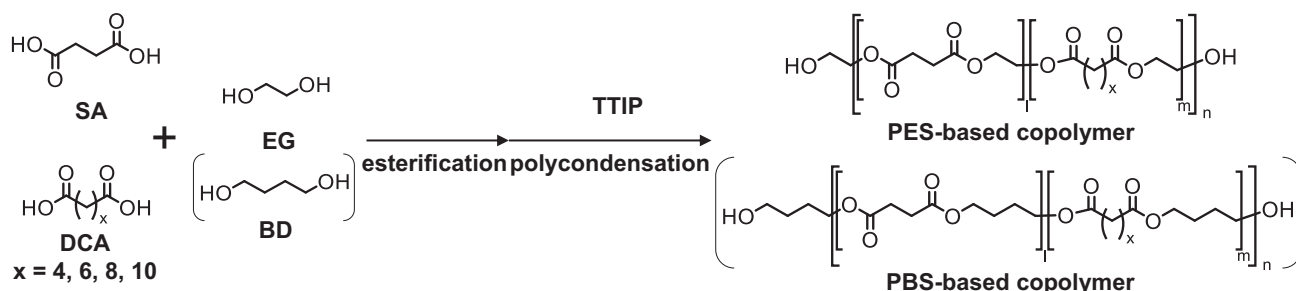
The molecular weights of the copolymers were analyzed via SEC at 40 °C.  $\text{CHCl}_3$  was used as the eluent with a flow rate of 0.8  $\text{mL min}^{-1}$ . Polystyrene standards with low polydispersities were used to prepare a calibration curve.

### TGA

TGA was conducted from room temperature to 500 °C under a nitrogen atmosphere at a heating rate of 10 °C  $\text{min}^{-1}$ . The 5% thermal decomposition temperature ( $T_{d5}$ ) was defined as the temperature at which the weight loss of the sample reached 5% of the total weight.

### DSC

The temperature and heat capacity of the instrument used for DSC measurements were calibrated with an indium calibration standard. The polymer samples were pressed between polytetrafluoroethylene (PTFE) sheets for 30 s at room temperature at 10 MPa. A piece (approximately 3 mg) of the obtained film was sealed in an aluminum pan. An empty pan was used as a reference. The measurements were performed as follows: First, the pan containing the sample and an empty pan were cooled to  $-70$  °C and heated to 140 °C at a rate of 20 °C  $\text{min}^{-1}$  and held there for 1 min. Then, the pans were cooled to  $-70$  °C at a rate of 200 °C  $\text{min}^{-1}$  and held there for 1 min, and heated to 140 °C at a rate of 20 °C  $\text{min}^{-1}$  once more. The melting point ( $T_m$ ) and glass transition temperature ( $T_g$ ) were measured during the first and second heating, respectively.



**Scheme 1** Syntheses of PES- and PBS-based copolyesters via two-step melt polycondensations of SA, DCA, and diols

### BOD biodegradability of polyester samples with seawater as an inoculum

Seawater from Hojo Beach (Chiba, Japan) was used as the inoculum in the BOD biodegradation tests. All tests were conducted at 25 °C with stirring in accordance with the ISO standard guideline (ISO 14851:1999).  $\text{CHCl}_3$  solutions containing the polymer samples (approximately 5 mg) were added to the BOD instrument, and cast films were prepared by removing the solvent. Next, four mineral stock solutions were prepared. Solution A contained 8.5 g L<sup>-1</sup>  $\text{KH}_2\text{PO}_4$ , 21.75 g L<sup>-1</sup>  $\text{K}_2\text{HPO}_4$ , 33.4 g L<sup>-1</sup>  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , and 0.5 g L<sup>-1</sup>  $\text{NH}_4\text{Cl}$ ; Solution B contained 22.5 g L<sup>-1</sup>  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; Solution C contained 36.4 g L<sup>-1</sup>  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ; and Solution D contained 0.25 g L<sup>-1</sup>  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . Then, 200 mL of seawater as an inoculum was added to 2 mL of Solution A and 0.2 mL of Solutions B, C, and D. At least two biodegradation tests were conducted on each polymer sample for 60 d, and the BOD data were measured once every 6 h. The biodegradabilities of the polymer samples were calculated by subtracting the BOD of the control blank ( $\text{BOD}_b$ ) from that of the test solution ( $\text{BOD}_t$ ) and dividing the value ( $\text{BOD}_t - \text{BOD}_b$ ) by the theoretical oxygen demand of the polymer samples.

### Tensile properties

Tensile tests were conducted with a crosshead speed of 10 mm min<sup>-1</sup> with dumbbell-shaped films (size of the measuring point: 4 × 10 mm<sup>2</sup>). The samples for the tensile tests were prepared via hot pressing between PTFE sheets for 1 min at 140 °C and 15 or 30 MPa to obtain films. The breaking point was defined as the point at which the decline in the test force reached 2% s<sup>-1</sup>. Five tests were performed for each polymer, and the results were averaged.

### WCA assay

Films of the polymer samples were prepared with the casting method. The polymer samples (357 mg) were dissolved in  $\text{CHCl}_3$  (15 mL) and dried on glass dishes. WCA

measurements were conducted on both sides of the obtained films using a 1.0 μL injection volume of pure water. Three tests were performed for each polymer, and the results were averaged.

### XRD

The films used for the WCA assay were then subjected to XRD measurements. Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm; 40 kV; 30 mA) was used as the source. The crystallinities of the obtained polymer films were calculated from the diffracted intensity data with Vonk's method [38].

### Hydrolytic degradation tests

The same set of films was subjected to hydrolytic degradation tests. Each film (10 × 10 mm<sup>2</sup>) was immersed in a screw-cap vial containing 5 mL of deionized water at 60 °C. After a certain period of time, each film was removed and weighed after washing and drying under reduced pressure. The molecular weights of the films were determined with SEC.

## Results and discussion

PES, PBS, and their copolymers were synthesized with a two-step process involving the esterification of SA, EG (or BD), and one DCA (AdA, SubA, SebA, and DDDA), followed by polycondensation with a titanium catalyst (Scheme 1). The obtained polymers were purified via reprecipitation.

The PES-based copolymers were synthesized at DCA/(SA + DCA) feed ratios of 20, 15, 10, and 5 mol%, whereas the PBS-based copolymers were synthesized at a DCA/(SA + DCA) feed ratio of 20 mol%. The DCA/(SA + DCA) molar ratios of the monomer feeds and their contents, as well as the yields, molecular weights, and thermal properties of the obtained polymers, are listed in Table 1. The <sup>1</sup>H NMR spectra of the PES-based copolymers containing DDDA units (PESDDD20, 15, 10, 5) are shown in Fig. 1 as

**Table 1** DCA/(SA + DCA) feed and content molar ratios, molecular weights, and thermal properties of the obtained polymers

Entry	Sample	DCA	Diol	DCA/(SA + DCA) <sup>a</sup> [mol%]	DCA/(SA + DCA) <sup>b</sup> [mol%]	Yield [%]	$M_n \times 10^{-3c}$ [g mol <sup>-1</sup> ]	$M_w \times 10^{-3c}$ [g mol <sup>-1</sup> ]	$\mathcal{D}^c$ [-]	$T_{d5}$ [°C]	$T_g$ [°C]	$T_m$ [°C]	$\Delta H_m$ [J g <sup>-1</sup> ]
1	PES	–	EG	0	0	44	70.0	113.6	1.6	323	–3.6	107	62.1
2	PESAd20	AdA	EG	20	24.8	61	67.7	103.3	1.5	317	–13.8	73	39.3
3	PESAd15	AdA	EG	15	18.7	59	65.2	101.7	1.6	323	–12.3	76	50.7
4	PESAd10	AdA	EG	10	12.5	52	73.1	119.6	1.6	329	–9.5	89	54.1
5	PESAd5	AdA	EG	5	6.3	51	69.4	121.3	1.7	318	–6.6	99	51.1
6	PESSub20	SubA	EG	20	25.0	62	64.2	98.9	1.5	329	–20.3	72	42.1
7	PESSub15	SubA	EG	15	20.3	56	68.3	105.6	1.5	329	–17.5	80	50.6
8	PESSub10	SubA	EG	10	13.4	56	61.7	98.4	1.6	325	–12.9	84	55.5
9	PESSub5	SubA	EG	5	6.5	50	68.0	123.5	1.8	324	–8.7	98	55.0
10	PESSeb20	SebA	EG	20	26.7	64	66.6	107.1	1.6	327	–24.5	68	39.8
11	PESSeb15	SebA	EG	15	21.1	58	61.1	102.8	1.7	325	–21.3	79	54.4
12	PESSeb10	SebA	EG	10	14.7	52	68.1	110.6	1.6	329	–16.8	85	53.4
13	PESSeb5	SebA	EG	5	7.0	51	67.0	114.0	1.7	332	–10.6	98	57.0
14	PESDDD20	DDDA	EG	20	28.6	61	86.4	196.1	2.3	336	N.D.	66	36.0
15	PESDDD15	DDDA	EG	15	21.5	58	71.5	131.1	1.8	332	–23.5	77	45.0
16	PESDDD10	DDDA	EG	10	15.2	52	78.5	128.1	1.6	329	–19.5	85	58.1
17	PESDDD5	DDDA	EG	5	7.2	50	73.9	129.6	1.8	334	–12.6	97	53.9
18	PBS	–	BD	0	0	72	99.5	169.5	1.7	343	N.D.	120	94.0
19	PBSAd20	AdA	BD	20	22.0	80	78.2	139.6	1.8	338	–40.3	95	57.4
20	PBSSub20	SubA	BD	20	22.3	79	71.7	126.4	1.8	341	–43.5	97	65.0
21	PBSSeb20	SebA	BD	20	21.9	82	91.2	154.7	1.7	334	–45.8	97	68.3
22	PBSDDD20	DDDA	BD	20	22.1	83	90.1	158.4	1.8	350	–43.5	95	69.6

<sup>a</sup>DCA/(SA + DCA) feed molar ratio<sup>b</sup>DCA/(SA + DCA) actual content molar ratio calculated using <sup>1</sup>H NMR<sup>c</sup> $M_w$ ,  $M_n$ , and molecular-weight distribution ( $\mathcal{D} = M_w/M_n$ ) determined using conventional SEC against PSt standards in CHCl<sub>3</sub>

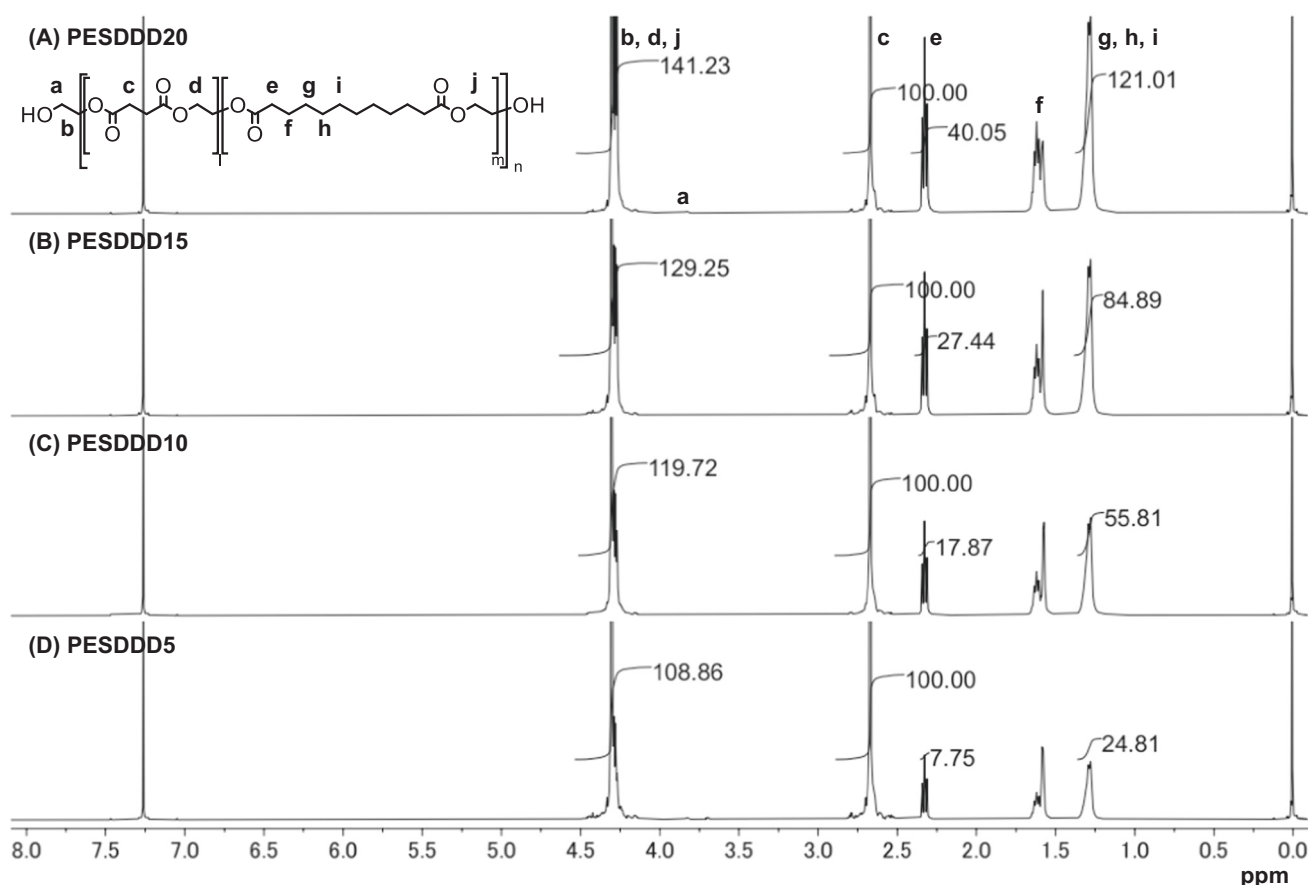
an example, and the <sup>1</sup>H and <sup>13</sup>C NMR spectra of all copolymers are shown in Figs. S1–S16. The DCA/(SA + DCA) content molar ratios for all polymers were higher than the feed ratios. Because white crystals were deposited on the reaction vessel and trapped after the reaction, the difference in the molar ratios for the monomer feed and polymer content may be due to sublimation of the succinic anhydride produced from SA by heating during the synthesis. The composition of the obtained polymer was confirmed with matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Figures S17–S20 show the peak intervals corresponding to the molecular weights of SA and EG or DCA and EG units, indicating that SA and DCA were copolymerized with EG.

The number-average molecular weight ( $M_n$ ) values of the obtained polymers were greater than  $60 \times 10^3$  g mol<sup>-1</sup>, and their weight-average molecular weights ( $M_w$ ) were close to or larger than  $100 \times 10^3$  g mol<sup>-1</sup>. Furthermore, the molecular weight distributions  $\mathcal{D}$  of most of the polymers were slightly less than 2.0 (Table 1, Fig. S21). Notably, the  $M_w$  of PESDDD20 synthesized from SA, EG, and DDDA at a DCA/(SA + DCA) feed ratio of 20 mol% was higher than that of the

other samples, and its  $\mathcal{D}$  was 2.3 (Table 1, entry 14). The  $M_w$  values for the PES-based copolymers containing DDDA tended to be higher than those of the copolymers containing other types of DCAs. Moreover, because the DCA/(SA + DCA) content molar ratio of PESDDD20 was higher than those of the other copolymers at the same feed ratio, PESDDD20 may have been more strongly affected by the molecular weight increase brought about by the DDDA units than the other polymers.

In terms of thermal stabilities, the  $T_{d5}$  values of PES and the PES-based copolymers ranged from 310 to 340 °C, while those of PBS and the PBS-based copolymers ranged from 330 to 350 °C (Fig. 2). Copolymerization demonstrated no significant influence on the thermal stabilities of the samples, which means that this property was independent of the DCA structure.

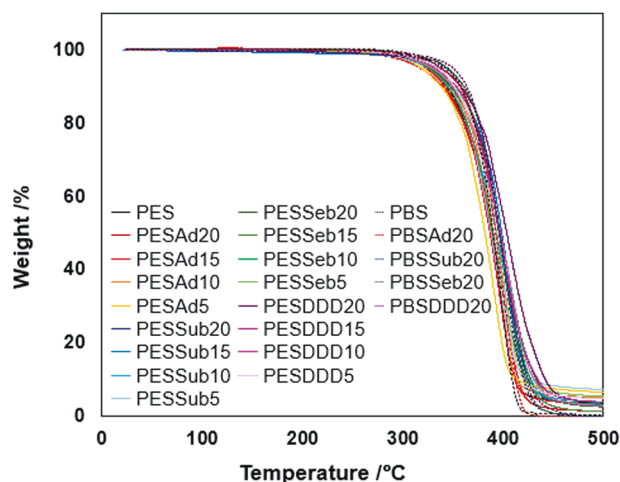
The  $T_m$  and  $T_g$  values of PES and the PES-based copolymers generally decreased with increasing DCA content (Fig. 3). The  $T_g$  of PESDDD20 was not detectable because it overlapped with the crystallization peak (Table 1, entry 14, Fig. 3). When the  $T_m$  and  $T_g$  values of the PES-based copolymers containing different lengths of DCA units at the same feed ratio were compared, the  $T_g$  decreased as the carbon number of the



**Fig. 1**  $^1\text{H}$  NMR spectra and peak assignments of PES-based copolymers containing DDA: (A) PESDDD20, entry 14 in Table 1; (B) PESDDD15, entry 15; (C) PESDDD10, entry 16; and (D) PESDDD5, entry 17

DCA increased, whereas  $T_m$  showed minimal changes [39–41]. The  $T_g$  of the PBS homopolymer could not be detected in the DSC thermogram owing to crystallization during cooling prior to the second heating scan (Fig. S22). However, both the  $T_m$  and  $T_g$  values of the PBS-based copolymers were lower than those of the PBS homopolymer reported in the literature [26, 27].

The results of the tensile tests are presented in Supplementary Information Table S1 and Figs. S23–S25. The tensile moduli of the PES-based copolymers decreased with increasing DCA content, whereas the strains at break increased with a few exceptions. Such changes in tensile moduli and strains at break were attributed to decreased crystallinities of the copolymers owing to the incorporation of DCA units into the PES molecules [30]. Compared with that of PES, the stresses at break of the PES-based copolymers first increased when DCA was added at a DCA/(SA + DCA) feed ratio of 5 mol% and then decreased as the amount of DCA was increased. The increase in the stresses at break following the incorporation of a small amount of DCA was explained by increases in the plasticities and strain hardening of the copolymers owing to changes in their chain



**Fig. 2** TGA curves of the obtained polymers

orientations [30]. Incorporation of more DCA into the PES molecules led to an increase in the amorphous regions and a decrease in the stresses at break. Similar to the results for the PES-based copolymers, decreases in tensile moduli and stresses at break and increases in strains at break were observed for the PBS-based copolymers.

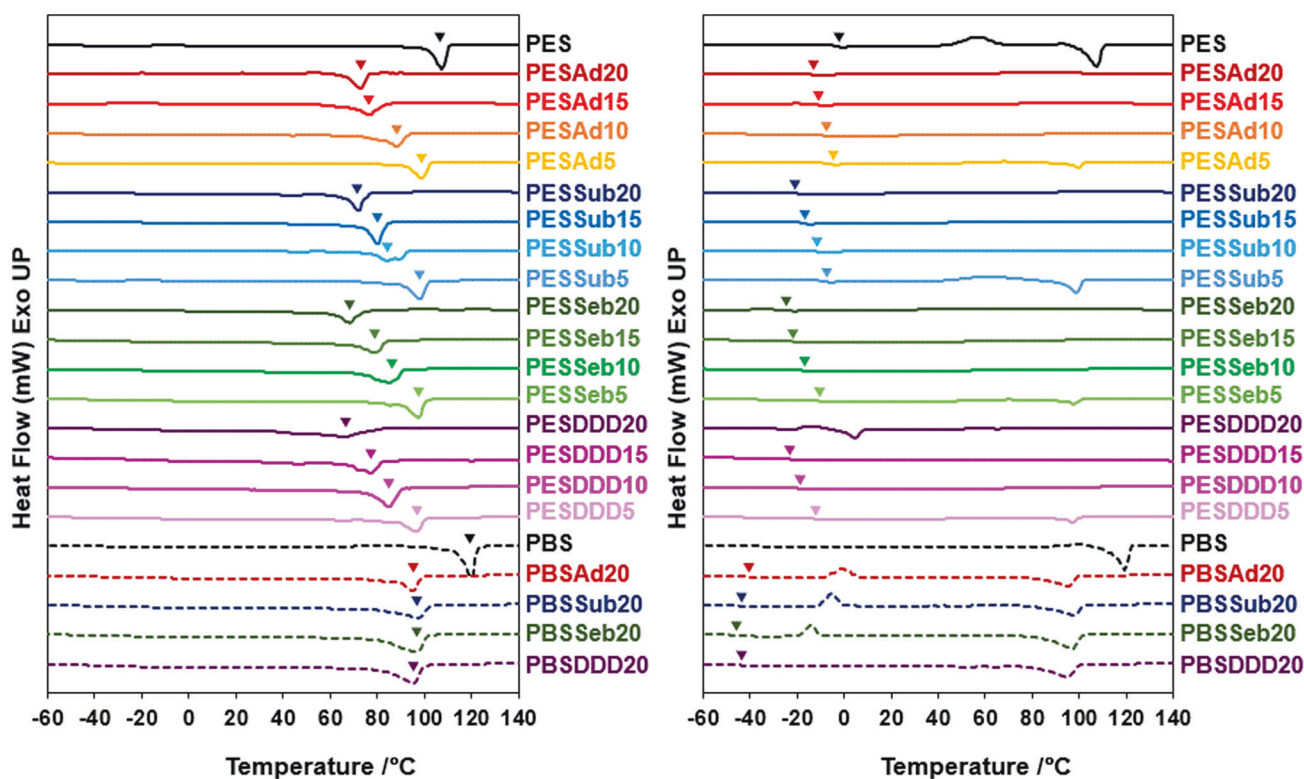


Fig. 3 DSC curves of the obtained polymers during the first (left) and second (right) heating scans

The results of the BOD biodegradation tests with the copolymers are shown in Fig. 4. Similar to previous reports [12], PES and PBS did not exhibit biodegradability even after 60 d (Fig. 4A). PES-based copolymers containing AdA were also insignificantly degraded in seawater, regardless of their AdA contents (Fig. 4B). In contrast, PES-based copolymers containing other DCAs exhibited biodegradability in seawater depending on the feed ratio. The BOD biodegradabilities of PES-based copolymers containing SubA synthesized at feed ratios of less than 10 mol% remained nearly unchanged for 60 d, whereas those of copolymers prepared at feed ratios with over 15 mol% SubA gradually increased after a two-week induction period (Fig. 4C). The biodegradation mechanism consisted of a decrease in the molecular weight via abiotic or enzymatic hydrolysis and mineralization of the decomposed low-molecular-weight components by microorganisms. Because the BOD biodegradabilities were calculated with the amount of consumed oxygen in the latter, cleavage of the polymer chain seemed to have occurred during the observed induction period. Changes in BOD biodegradabilities, which began after a short induction period of 5 d, were observed for the PES-based copolymers synthesized at feed ratios of over 10 mol% SebA (Fig. 4D). The BOD biodegradabilities of PESSeb15 and PESSeb20 reached constant values (approximately 70%) within 30 d. The

major components (approximately 70%) of the copolymers were utilized by microorganisms for energy generation, whereas the minor components (approximately 30%) were used for biomass formation. The BOD biodegradability of PESSeb10 gradually increased over time, reaching approximately 60% after 60 d. A longer time was needed to completely degrade PESSeb10. The biodegradation of PES-based copolymers containing DDDA began at an earlier time, and the BOD biodegradabilities of samples prepared with feed ratios greater than 10 mol% DDDA reached constant values within 20 d (Fig. 4E). In addition, although the reaction proceeded slowly, PESDDD5 was eventually biodegraded in seawater. Thus, the incorporation of DCAs with larger numbers of carbon atoms into the PES molecules induced efficient biodegradation in seawater. As shown in Fig. 4F, the incorporation of SebA or DDDA units into the PBS-based copolymers led to marine biodegradability, whereas the incorporation of AdA or SubA brought about minimal changes in this characteristic.

Figure 5 shows plots of the BOD biodegradabilities of the copolymers obtained after 60 d as functions of their DCA/(SA + DCA) content molar ratios (Fig. 5A, C) and weight ratios (Fig. 5B, D). The method used to calculate the content weight ratios is described in the Supplementary Information. A linear relationship between the BOD biodegradabilities and the DCA composition was not

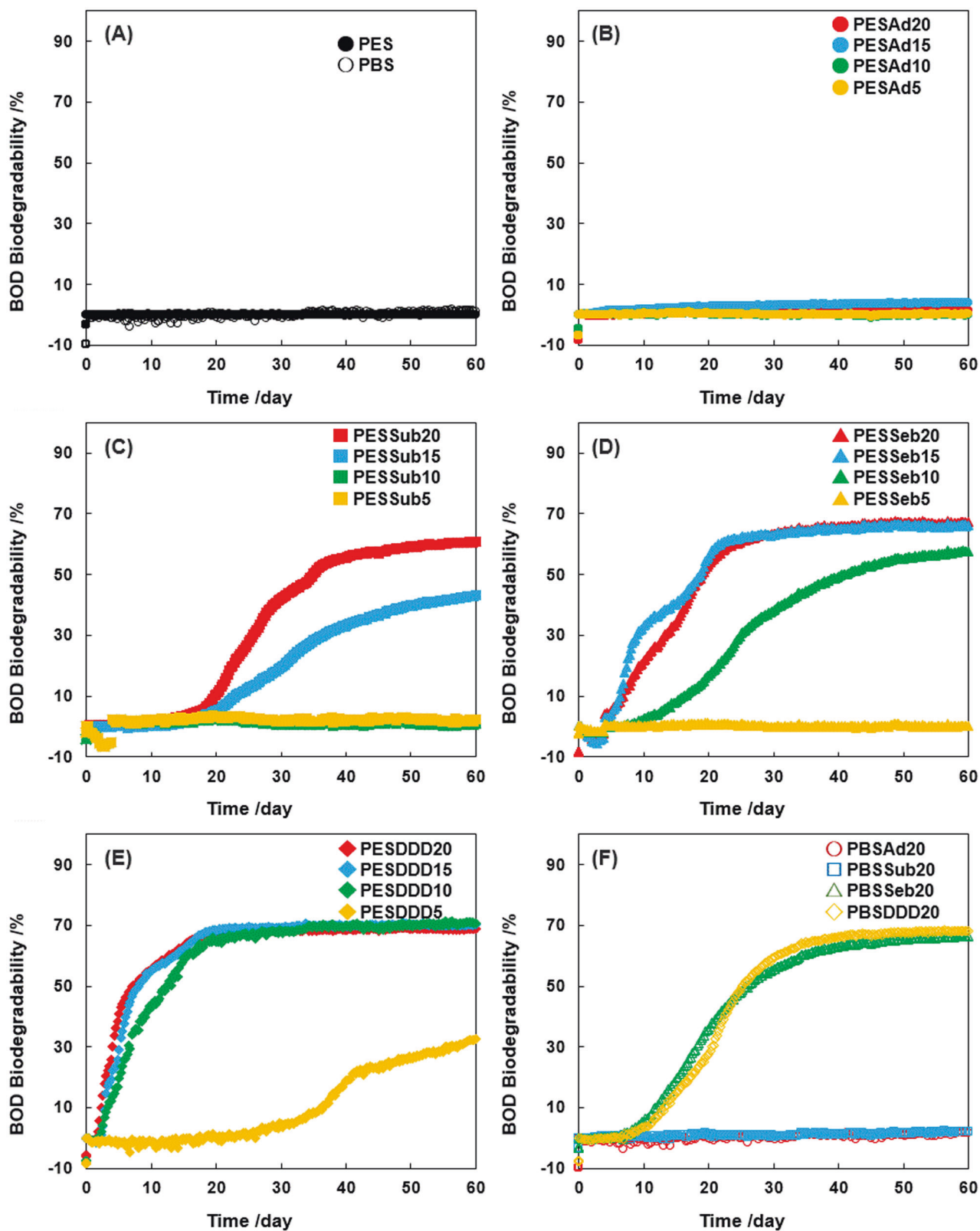
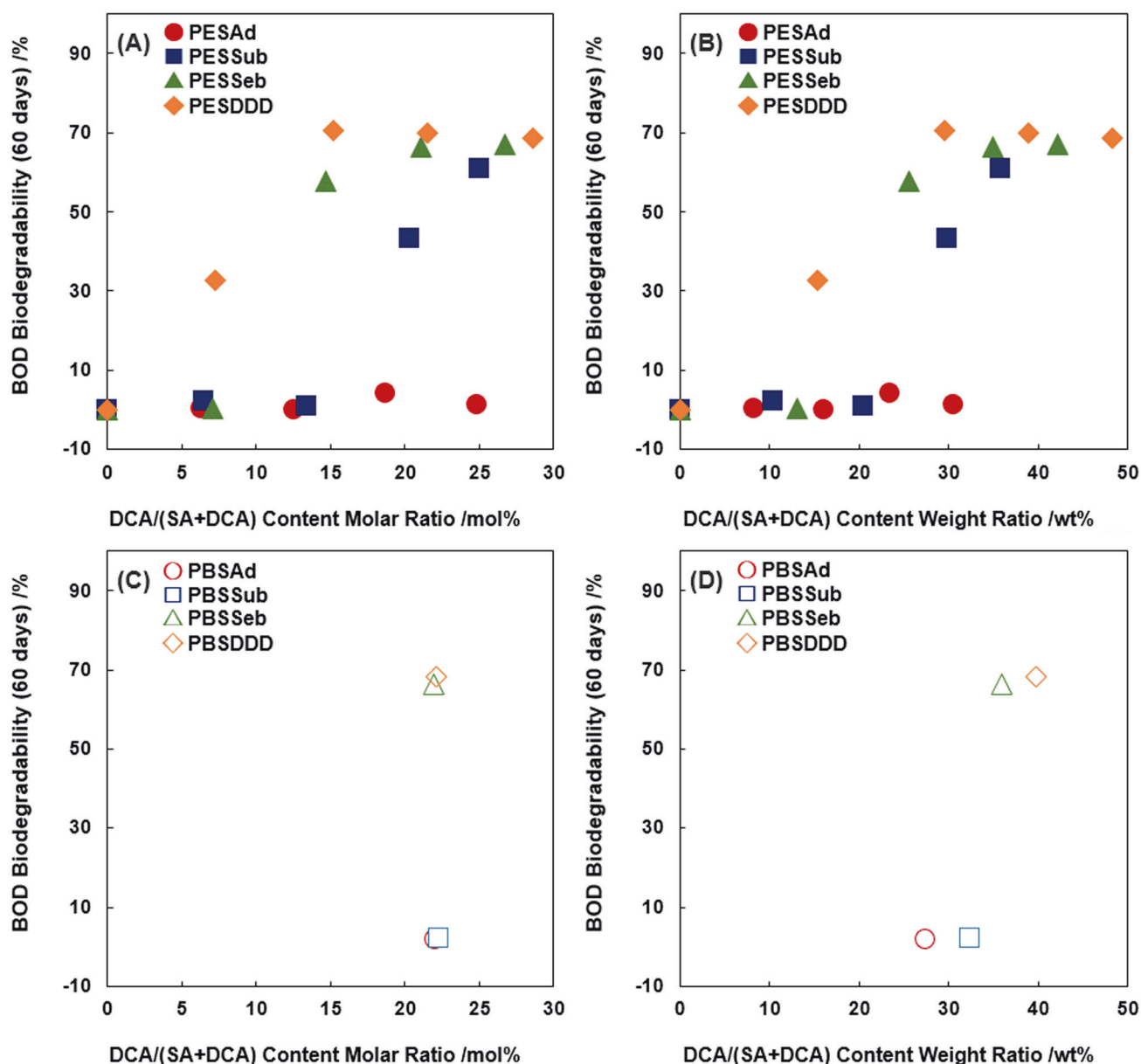


Fig. 4 BOD biodegradation curves of the obtained polymers: (A) PES and PBS; (B) PESAd20, 15, 10, 5; (C) PESSub20, 15, 10, 5; (D) PESSeb20, 15, 10, 5; (E) PESDDD20, 15, 10, 5; and (F) PBS-based copolymers





**Fig. 5** DCA/(SA + DCA) content molar or weight ratios and 60-day biodegradabilities of the obtained polymers: (A, B) PES-based copolymers (molar and weight ratios) and (C, D) PBS-based copolymers (molar and weight ratios)

observed for the PES- and PBS-based copolymers. However, the marine biodegradabilities of these polyesters improved after the incorporation of small amounts of longer-chain DCAs. The incorporation of longer-chain DCAs increased the mobilities of the polymer chains, as evidenced by the lower  $T_g$  values. However, the  $T_g$  for marine biodegradable PESDDD5 was similar or slightly higher than that for PESAd20, suggesting that the effect of the DCAs on marine biodegradabilities was not limited to mobility changes in the polymer chains. To investigate the effects of incorporating DCAs on the crystallinities and hydrophobicities of the obtained polymers, we conducted

XRD and WCA measurements and hydrolytic degradation tests. The WCAs and crystallinities are listed in Table S2. Moreover, Fig. S26 shows the XRD patterns, and Figs. S27 and 28 display the changes in  $M_w$  after hydrolytic degradation. Overall, the WCA decreased as the amount of DCA was increased, suggesting improved surface hydrophilicity. However, the WCAs of the marine biodegradable polymers containing DCAs, such as DDDA and SebA, were larger than those of nonmarine biodegradable PESAd20. The WCA was greatly influenced by the composition and surface shape, and no clear correlation with marine biodegradabilities was observed. The crystallinities of the

obtained polymers decreased as the amount of DCA was increased, but poorly crystalline polymers did not necessarily exhibit marine biodegradability. No significant difference in hydrolysis activity was observed among the obtained polymers in the hydrolytic degradation tests. Therefore, the incorporation of longer-chain DCAs may have played other roles, such as improving the enzyme affinity, in addition to reducing the crystallinity or influencing the hydrophobicity [42].

## Conclusion

In this study, PES- and PBS-based copolymers containing DCA units with various carbon numbers were synthesized, and their thermomechanical properties and the marine biodegradabilities were investigated. The  $T_m$  and  $T_g$  values generally decreased with increasing DCA content. At the same feed ratio,  $T_g$  decreased as the number of carbon atoms in the DCA increased, whereas  $T_m$  remained relatively constant. Tensile tests of the PES-based copolymers showed decreases in the tensile moduli and increases in the strains at break with increasing DCA contents. The stresses at break of the copolymers with small amounts of DCA incorporated initially increased compared with that of PES and decreased with further increases in the DCA content. Copolymers with long-chain DCA units appeared to exhibit marine biodegradability, even at low DCA contents. These results indicated that the thermomechanical properties and the marine biodegradabilities of the PES- and PBS-based copolymers could be regulated by controlling their structures and DCA contents. The results of this study could facilitate copolymerization of DCA with other polymers, including aromatic polyesters and poly(ester amide)s, and lead to the development of marine biodegradable polymers with optimal properties that make them suitable for general-purpose applications such as bottles, packaging, films, and fishing equipment. At present, the limitations of marine biodegradable polymers include a narrow range and sub-optimal biodegradation properties; hence, further research on strategies to improve the structures and properties of these polymers should be conducted. Overall, the results of this work may contribute to expansion of the future applications of these polymers.

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## Compliance with ethical standards

**Conflict of interest** The authors declare no competing interests.

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