

Article

Enzymatic Synthesis and Chemical Recycling of Novel Polyester-Type Thermoplastic Elastomers

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Abstract: Novel polyester-type thermoplastic elastomers based on poly(alkylene succinate)s were synthesized by the lipase-catalyzed copolymerization of cyclic diol/succinate oligomer and cyclic diol/alkylthiosuccinate oligomer. These copolymers exhibited biodegradabilities by activated sludge and a wide range of thermal and mechanical properties that were dependent on the molecular structure and the content of side alkylthio groups. The degree of crystallinity of the copolymer decreased with increasing content of alkylthio groups, which were introduced into the polymer chain as a soft segment. Furthermore, lipase-catalyzed depolymerization of these copolymers into cyclic oligomers and repolymerization of the oligomers was carried out. A repolymerized copolymer having the same M_w and monomer composition as the initial copolymer was obtained, indicating the chemical recyclability of the copolymer.

Keywords: biobased polyester; biodegradable; chemical recycling; environmentally benign thermoplastic elastomer; lipase-catalyzed polymerization

1. Introduction

Thermoplastic elastomers (TPE) are widely used as soft materials for industrial and medical applications. Unlike crosslinked-type elastomers, TPEs show thermoplasticity and can be easily recycled with remolding of the parent material. The typical example of a TPE is the ethylene- α -olefin copolymer, consisting of a polyethylene main chain and an alkyl side chain unit. The main chain acts

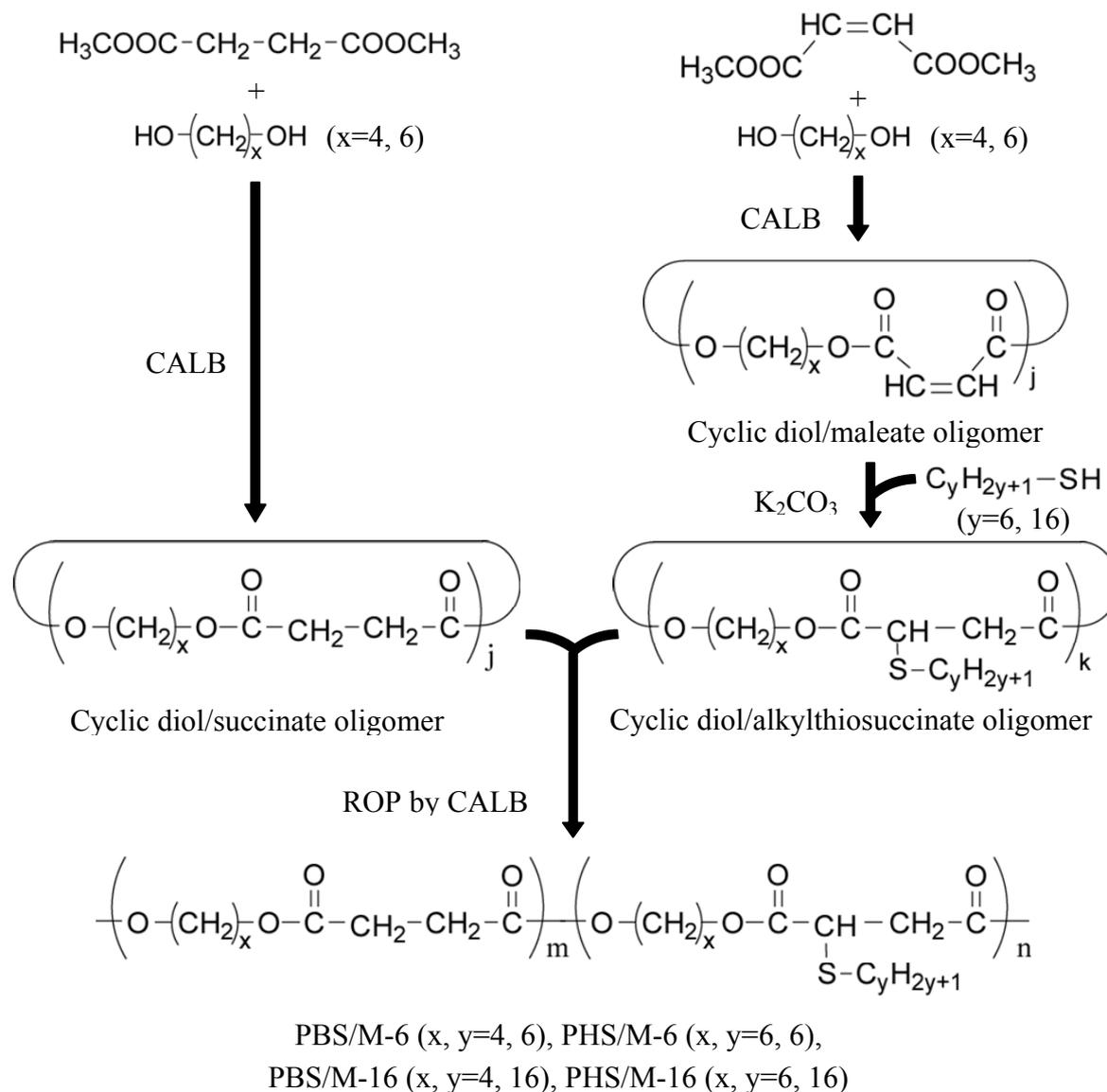
as the hard segment because of its high crystallinity, while the alkyl side chain unit acts as the soft segment due to its steric hindrance to crystallization. The degree of crystallinity decreases with increasing content of soft segments; thus, the polymer changes from a rigid plastic to a soft elastomer [1–3].

In the field of elastomers, environmentally benign properties become more important [4,5]. Examples of such properties include the replacement of petrochemical resources by bio-based resources, biodegradability and chemical recyclability. However, environmentally benign elastomers have not been developed yet. Currently available TPEs, such as ethylene- α -olefin copolymer, are only produced from petrochemicals and are highly resistant to biodegradation.

Thus, for the next generation of elastomers, establishment of an environmentally benign production method is an important issue. In recent years, enzymatic synthesis has been studied as a novel and green methodology for polymer production. Enzymes are renewable and nontoxic catalysts with high catalytic activities. For example, lipases can act as powerful catalysts for polyesterification reactions under mild anhydrous conditions. The syntheses of high molecular weight polyesters by ring-opening polymerization (ROP) of cyclic oligomers have also been reported [6–9]. In addition, using a lipase as the catalyst in anhydrous dilute solution, polyesters can be easily depolymerized into repolymerizable cyclic oligomers. In such a way, lipases may also contribute to the establishment of sustainable polymer production and chemical recycling systems [10–12].

Diol/diacid-type aliphatic polyesters are typical polymers that can be readily produced and chemically recycled by lipases. It is reported that poly(butylene succinate) (PBS) and poly(hexamethylene succinate) (PHS) are produced by the lipase-catalyzed polymerization of succinic acid with butane-1,4-diol and hexane-1,6-diol, respectively [13,14]. The polymers exhibit good biodegradability and can be considered to be bio-based plastics, because succinic acid can be produced by fermentation, and butane-1,4-diol and hexane-1,6-diol can be produced by the reduction of bio-based succinic acid and adipic acid, respectively. However, the impact strength of PBS is relatively low, preventing its use in various applications.

One effective way to resolve this problem is to form PBS-based thermoplastic elastomers by the introduction of soft segments into the polymer chain [15–18]. The impact strength may be increased, and also such elastomers are expected to be biodegradable and chemically recyclable. In this study, a series of polyester-type elastomers consisting of PBS and PHS moieties as the hard segment and an alkyl side chain unit as the soft segment were prepared by the lipase-catalyzed copolymerization of cyclic oligomers as shown in Scheme 1. Their thermal and mechanical properties, biodegradabilities and chemical recyclabilities were evaluated.

Scheme 1. Enzymatic synthesis of novel thermoplastic elastomers.

2. Experimental Section

2.1. Materials

Dimethyl succinate, dimethyl maleate, butane-1,4-diol, hexane-1,6-diol and 1-hexanethiol were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). 1-Hexadecanethiol was purchased from TCI Co., Inc. (Tokyo, Japan). Immobilized lipase from *Candida antarctica* was kindly supplied by Novozymes Japan, Ltd. [Chiba, Japan; CALB: Novozym 435, a lipase (lipase B) from *C. antarctica* produced by submerged fermentation of a genetically modified *Aspergillus oryzae* microorganism and absorbed on a macroporous acrylic resin (10000 propyl laurate units per gram; lipase activity based on ester synthesis)]. The enzyme was dried under vacuum (3 mmHg) over P₂O₅ at 25 °C for 2 h before use. Molecular sieves 4A were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA) and were dried at 120 °C for 2 h before use.

2.2. Measurements

The weight-average (M_w) and number-average (M_n) molecular weight and the molecular weight distribution (M_w/M_n) of the polymer were determined by size exclusion chromatography (SEC) using SEC columns (Shodex K-805L + K-800D, Showa Denko Co., Ltd., Tokyo, Japan) with a refractive index detector; chloroform was used as the eluent at $1.0 \text{ mL}\cdot\text{min}^{-1}$. The SEC system was calibrated with polystyrene standards of a narrow molecular weight distribution. The molecular weight of the oligomers was measured by matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) using a Bruker Ultraflex mass spectrometer equipped with a nitrogen laser. The detection was performed in the reflection mode, a cobalt matrix was used for oligomers, sodium bromide was used as a cation source, and positive ionization was used. ^1H NMR spectra were recorded on a Varian 300 Fourier transform spectrometer (Varian Inc., CA, USA) operating at 300 MHz.

The crystallization temperature (T_c), melting temperature (T_m) and glass transition temperature (T_g) of the polymer were determined by differential scanning calorimetry (DSC-60, Shimadzu Co., Kyoto, Japan). The measurements were made with a sample (10 mg) on a DSC plate. The polymer samples were heated at a rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from $30 \text{ }^\circ\text{C}$ to $120 \text{ }^\circ\text{C}$ (first scan), cooled at a rate of $-30 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $-80 \text{ }^\circ\text{C}$ and then scanned with heating at a rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $120 \text{ }^\circ\text{C}$. Wide angle X-ray diffraction (WAXD) patterns were obtained using Ni-filtered $\text{Cu-K}\alpha$ radiation at room temperature. A voltage and current of X-ray source were set to be 40 kV and 40 mA. Crystallinity (χ_c) of the films was calculated from diffracted X-ray intensity data in the 2θ range of $5\text{--}40^\circ$ using the calculation program (DISCOVER, Bruker AXS K.K., Yokohama, Japan). The mechanical properties of the film samples were determined by an Autograph instrument (Shimadzu Co., Kyoto, Japan) at the cross-head speed of $30 \text{ mm}\cdot\text{min}^{-1}$.

The biodegradability of the copolymers was evaluated by biochemical oxygen demand (BOD) measurements. BOD was determined with a BOD tester (VELP Scientifica s.r.l., Usmate, MI, Italy) by the oxygen consumption method, according to the modified MITI test. The activated sludge was obtained from a municipal sewage plant in Yokohama City. BOD biodegradation (BOD/ThOD) was calculated from the BOD values and the theoretical oxygen demand (ThOD).

2.3. Enzymatic Synthesis of Novel Thermoplastic Elastomer

2.3.1. Preparation of Cyclic Diol/Succinate Oligomer

The cyclization was carried out in a round-bottomed flask with molecular sieves 4A placed at the top of the flask in the vapor phase to absorb the byproducts. In a typical procedure, dimethyl succinate (73 mg; 0.50 mmol) and butane-1,4-diol (48 mg; 0.53 mmol) were reacted by CALB (121 mg; 100 wt.%) as the catalyst in toluene (24 mL; $5.0 \text{ mg}\cdot\text{mL}^{-1}$) under a nitrogen atmosphere at $90 \text{ }^\circ\text{C}$ for 48 h.

The reaction mixture was diluted with chloroform, and the CALB was removed by filtration. The solvent was then evaporated under reduced pressure to obtain cyclic butylene/succinate (BS) oligomer. The crude product was purified by column chromatography (silica gel 60N, 40 g) using chloroform-ethyl acetate (6:1 v/v, $R_f = 0.40$) as an eluent to obtain cyclic BS dimer as white crystals in 44% yield. In a

similar procedure, cyclic hexamethylene/succinate (HS) dimer was produced by the reaction of dimethyl succinate and hexane-1,6-diol in 36% yield.

Cyclic BS dimer: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 1.66–1.76 [4H, m, $-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-$], 2.60–2.69 [4H, m, $-(\text{C}=\text{O})(\text{CH}_2)_2(\text{C}=\text{O})-$], 4.05–4.20 [4H, m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$]. m.p.: 114–116 °C.

Cyclic HS dimer: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 1.31–1.45 [4H, m, $-(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_2-$], 1.54–1.71 [4H, m, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{CH}_2-$], 2.59–2.67 [4H, m, $-(\text{C}=\text{O})(\text{CH}_2)_2(\text{C}=\text{O})-$], 4.10 [4H, t, $J = 6.6$ Hz, $-\text{OCH}_2(\text{CH}_2)_4\text{CH}_2\text{O}-$]. m.p.: 57–59 °C.

2.3.2. Preparation of Cyclic Diol/Maleate Oligomer

In a typical procedure, dimethyl maleate (72 mg; 0.50 mmol) and butane-1,4-diol (48 mg; 0.53 mmol) were reacted by CALB (120 mg; 100 wt.%) as the catalyst in toluene (24 mL; $5.0 \text{ mg}\cdot\text{mL}^{-1}$) under a nitrogen atmosphere at 90 °C for 48 h. The solvent was evaporated under reduced pressure. The reaction mixture was diluted with chloroform, and the CALB was removed by filtration to obtain cyclic butylene/maleate (BM) oligomer.

In a similar procedure, cyclic hexamethylene/maleate (HM) oligomer was produced by the reaction of dimethyl maleate and hexane-1,6-diol.

2.3.3. Preparation of Cyclic Diol/Alkylthiosuccinate Oligomer

The addition of thiol was carried out in a round-bottomed flask. In a typical procedure, a mixture of cyclic BM oligomer (170 mg; 1.0 mmol), 1-hexanethiol (118 mg; 1.0 mmol) and K_2CO_3 (51 mg; 30 wt.%) as the catalyst was stirred in dry acetone (2.9 mL; $100 \text{ mg}\cdot\text{mL}^{-1}$) and reacted under an argon atmosphere at 25 °C for 24 h.

The reaction mixture was diluted with chloroform, and K_2CO_3 was removed by filtration. The solvent was evaporated under reduced pressure to obtain cyclic butylene/hexylthiosuccinate (BM-6) oligomer. In a similar procedure, cyclic hexamethylene/hexylthiosuccinate (HM-6), cyclic butylene/hexadecylthiosuccinate (BM-16) and hexamethylene/hexadecylthiosuccinate (HM-16) oligomers were obtained.

The crude product was purified by column chromatography (silica gel 60N, 40 g) using hexane-ethyl acetate (6:1 v/v, $R_f = 0.38$) as the eluent to obtain cyclic BM-6 dimer and cyclic HM-6 monomer as liquids in 38% and 37% yields, respectively. In the case of the addition of 1-hexadecanethiol, a mixed solvent of hexane/chloroform/acetone (6:1:1 v/v/v, $R_f = 0.53$) was used as the eluent to obtain cyclic BM-16 dimer and HM-16 monomer as white crystals in 36% and 34% yields, respectively.

Cyclic BM-6 dimer: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.88 (3H, t, $J = 6.9$ Hz, CH_3CH_2-), 1.20–1.43 [6H, m, $\text{CH}_3(\text{CH}_2)_3\text{CH}_2-$], 1.50–1.68 (2H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$), 1.76–1.96 [4H, m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$], 2.52–2.92 (2H, m, $-\text{SCH}_2\text{CH}_2-$), 2.71 [1H, dd, $J = 11.4, 14.1$ Hz, $-\text{C}(\text{=O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 2.83 [1H, dd, $J = 6.0, 14.1$ Hz, $-\text{C}(\text{=O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 3.72 [1H, dd, $J = 6.0, 11.4$ Hz, $-\text{CH}_2\text{C}(\text{S}-)\text{H}(\text{C}=\text{O})-$], 4.12–4.38 [4H, m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$]. $\text{C}_{14}\text{H}_{24}\text{O}_4\text{S}$ (288.41): Calcd. C 58.30, H 8.39, S 11.12; Found C 58.37, H 8.58, S 11.14.

Cyclic HM-6 monomer: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.88 (3H, t, $J = 6.9$ Hz, CH_3CH_2-), 1.20–1.43 [6H, m, $\text{CH}_3(\text{CH}_2)_3\text{CH}_2-$], 1.44–1.84 [10H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$, $-\text{OCH}_2(\text{CH}_2)_4\text{CH}_2\text{O}-$],

2.57–2.74 (2H, m, $-\text{SCH}_2\text{CH}_2-$), 2.70 [1H, dd, $J = 3.6, 16.2$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 2.99 [1H, dd, $J = 12.3, 16.2$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 3.67 [1H, dd, $J = 3.6, 12.3$ Hz, $-\text{CH}_2\text{C}(\text{S}-)\text{H}(\text{C}=\text{O})-$], 4.10–4.26 [3H, m, $-\text{OCH}_2(\text{CH}_2)_4\text{C}(\text{H})\text{HO}-$], 4.43 [1H, ddd, $J = 3.3, 7.8, 11.7$, $-\text{OCH}_2(\text{CH}_2)_4\text{C}(\text{H})\text{HO}-$]. $\text{C}_{16}\text{H}_{28}\text{O}_4\text{S}$ (316.46): Calcd. C 60.73, H 8.92, S 10.13; Found C 60.65, H 9.07, S 10.40.

Cyclic BM-16 dimer: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.88 (3H, t, $J = 6.6$ Hz, CH_3CH_2-), 1.16–1.42 [26H, m, $\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2-$], 1.52–1.65 (2H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$), 1.78–1.93 [4H, m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$], 2.55–2.66 (2H, m, $-\text{SCH}_2\text{CH}_2-$), 2.69 [1H, dd, $J = 11.4, 14.4$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 2.82 [1H, dd, $J = 6.0, 14.4$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 3.72 [1H, dd, $J = 6.0, 11.4$ Hz, $-\text{CH}_2\text{C}(\text{S}-)\text{H}(\text{C}=\text{O})-$], 4.14–4.33 [4H, m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$]. $\text{C}_{24}\text{H}_{44}\text{O}_4\text{S}$ (428.68): Calcd. C 67.24, H 10.35, S 7.48; Found C 67.58, H 10.43, S 7.44. m.p.: 62–64 °C.

Cyclic HM-16 monomer: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.88 (3H, t, $J = 6.9$ Hz, CH_3CH_2-), 1.18–1.42 [26H, m, $\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2-$], 1.45–1.54 (2H, m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$), 1.54–1.84 [6H, m, $-\text{OCH}_2(\text{CH}_2)_4\text{CH}_2\text{O}-$], 2.58–2.70 (2H, m, $-\text{SCH}_2\text{CH}_2-$), 2.70 [1H, dd, $J = 3.6, 15.9$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 2.99 [1H, dd, $J = 12.6, 15.9$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 3.67 [1H, dd, $J = 3.6, 12.6$ Hz, $-\text{CH}_2\text{C}(\text{S}-)\text{H}(\text{C}=\text{O})-$], 4.15–4.35 [3H, m, $-\text{OCH}_2(\text{CH}_2)_4\text{C}(\text{H})\text{HO}-$], 4.43 [1H, ddd, $J = 3.3, 7.5, 10.8$, $-\text{OCH}_2(\text{CH}_2)_4\text{C}(\text{H})\text{HO}-$]. $\text{C}_{26}\text{H}_{48}\text{O}_4\text{S}$ (456.73): Calcd. C 68.37, H 10.59, S 7.02; Found C 68.13, H 10.86, S 6.94. m.p.: 40–42 °C.

2.3.4. Lipase-Catalyzed ROP of Cyclic Oligomers

The ROP was carried out in a screw-capped vial with molecular sieves 4A placed at the top of the vial in the vapor phase. In a typical procedure, cyclic BS dimer (29.1 mg) and cyclic BM-6 dimer (20.9 mg) were copolymerized in the presence of CALB (25 mg; 50 wt.%) under a nitrogen atmosphere at 120 °C for 24 h. The polymerization mixture was diluted with chloroform, and the CALB was removed by filtration. The purification was carried out by reprecipitation using chloroform (good solvent)/1-propanol (poor solvent) to obtain PBS/M-6 in 68% yield.

PBS/M-6: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.89 (t, $J = 5.7$ Hz, CH_3CH_2-), 1.19–1.42 [m, $\text{CH}_3(\text{CH}_2)_3\text{CH}_2-$], 1.50–1.64 (m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$), 1.64–1.82 [m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$], 2.53–2.75 [m, $-\text{SCH}_2\text{CH}_2-$, $-\text{C}(=\text{O})(\text{CH}_2)_2(\text{C}=\text{O})-$], 2.67 [dd, $J = 5.7, 17.1$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 2.99 [dd, $J = 9.6, 17.1$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 3.64 [dd, $J = 5.7, 9.6$ Hz, $-\text{CH}_2\text{C}(\text{S}-)\text{H}(\text{C}=\text{O})-$], 4.04–4.24 [m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$].

PHS/M-6: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.88 (t, $J = 6.9$ Hz, CH_3CH_2-), 1.21–1.49 [m, $\text{CH}_3(\text{CH}_2)_3\text{CH}_2-$, $-(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_2-$], 1.52–1.74 [m, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$], 2.55–2.76 [m, $-\text{SCH}_2\text{CH}_2-$, $-\text{C}(=\text{O})(\text{CH}_2)_2(\text{C}=\text{O})-$], 2.67 [dd, $J = 5.4, 10.8$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 2.99 [dd, $J = 9.6, 10.8$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 3.64 [dd, $J = 5.4, 9.6$ Hz, $-\text{CH}_2\text{C}(\text{S}-)\text{H}(\text{C}=\text{O})-$], 4.08–4.20 [br t, $-\text{OCH}_2(\text{CH}_2)_4\text{CH}_2\text{O}-$].

PBS/M-16: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.88 (t, $J = 6.6$ Hz, CH_3CH_2-), 1.15–1.42 [m, $\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2-$], 1.46–1.64 (m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$), 1.64–1.78 [m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$], 2.55–2.67 [m, $-\text{SCH}_2\text{CH}_2-$, $-\text{C}(=\text{O})(\text{CH}_2)_2(\text{C}=\text{O})-$], 2.67 [dd, $J = 5.7, 16.8$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 2.99 [dd, $J = 9.9, 16.8$ Hz, $-\text{C}(=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 3.63 [dd, $J = 5.7, 9.9$ Hz, $-\text{CH}_2\text{C}(\text{S}-)\text{H}(\text{C}=\text{O})-$], 4.02–4.23 [m, $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$].

PHS/M-16: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.88 (t, $J = 6.9$ Hz, CH_3CH_2-), 1.15–1.43 [m, $\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2-$, $-(\text{CH}_2)_2(\text{CH}_2)_2(\text{CH}_2)_2-$], 1.55–1.78 [m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{CH}_2-$], 2.52–2.72 [m, $-\text{SCH}_2\text{CH}_2-$, $-(\text{C}=\text{O})(\text{CH}_2)_2(\text{C}=\text{O})-$], 2.67 [dd, $J = 5.7, 17.1$ Hz, $-\text{C}(\text{C}=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 2.99 [dd, $J = 9.9, 17.1$ Hz, $-\text{C}(\text{C}=\text{O})\text{C}(\text{H})\text{HC}(\text{S}-)\text{H}-$], 3.63 [dd, $J = 5.7, 9.9$ Hz, $-\text{CH}_2\text{C}(\text{S}-)\text{H}(\text{C}=\text{O})-$], 3.90–4.23 [br t, $-\text{OCH}_2(\text{CH}_2)_4\text{CH}_2\text{O}-$].

2.4. Chemical Recycling of Polymers

The degradation was carried out in a round-bottomed flask with molecular sieves 4A placed at the top of the flask in the vapor phase to absorb the byproducts. In a typical procedure, PBS/M (100 mg) and CALB (100 mg; 100 wt.%) were stirred with toluene (20 mL; $5 \text{ mg}\cdot\text{mL}^{-1}$) and reacted under a nitrogen atmosphere at 100°C for 72 h. The reaction mixture was diluted with chloroform, and the CALB was removed by filtration to obtain degradation products consisting of cyclic oligomers.

The degradation products were subjected to repolymerization without any purification. The reaction was carried out by a method similar to the ROP of cyclic oligomers noted above.

3. Results and Discussion

3.1. Preparation of Cyclic Oligomers

Cyclic diol/succinate oligomers (cyclic BS and HS) as the hard segment were prepared by the cyclization of dimethyl succinate and diols with CALB in dilute toluene solution. A slight excess of diols was required in order to prevent production of species having terminal succinate ends, which were difficult to isolate from the cyclic oligomers. Cyclic diol/alkylthiosuccinate oligomers (cyclic BM-6, HM-6, BM-16 and HM-16) as the soft segment were prepared by the cyclization of dimethyl maleate and diols, followed by the addition of thiols in the presence of K_2CO_3 in acetone solution.

These cyclic oligomers were successfully isolated by silica gel column chromatography. The $^1\text{H-NMR}$ spectra supported the cyclic structures in that the terminal methyl ester and hydroxyl group disappeared after the reaction. Ring size of the cyclic oligomers was determined by MALDI-TOF MS spectrometry. As shown in Table 1, the main components of the cyclic oligomers were dimers or monomers. Relatively higher melting points of cyclic BS and HS suggest that the diol/succinate oligomers have crystallinity; therefore, they are expected to act as the hard segment of the copolymer. Also, cyclic BM-16 and HM-16 were crystals, while cyclic HM-6 and BM-6 were liquids at room temperature as shown in Table 1. These results indicate that hexyl side chains disturb the crystallization process; however, hexadecyl side chains might crystallize with their packing effect.

Table 1. Main components, yields and melting points of cyclic oligomers.

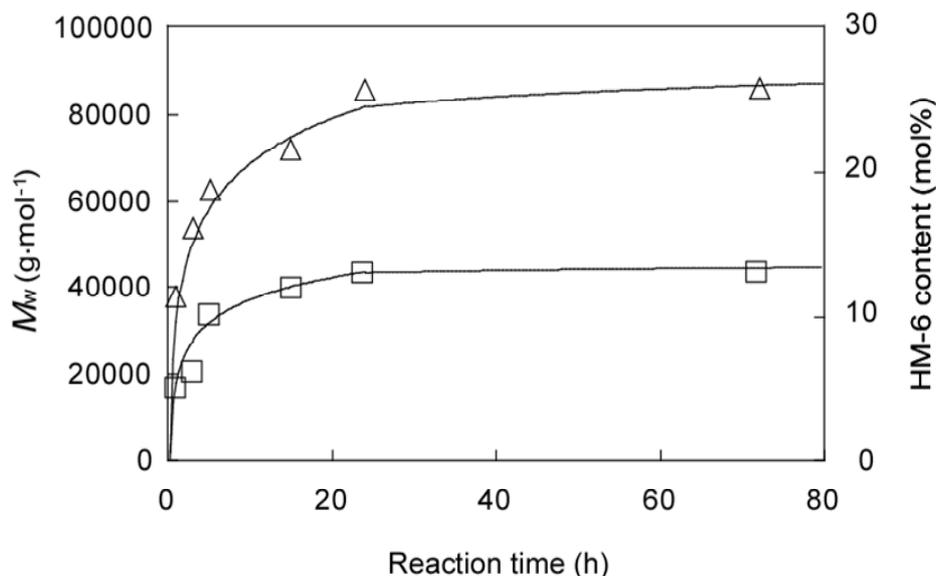
Cyclic Oligomer	Ring Size	Yield (%)	m.p. ($^\circ\text{C}$)
BS	Dimer	44	114–116
HS	Dimer	36	57–59
BM-6	Dimer	38	–
HM-6	Monomer	37	–
BM-16	Dimer	36	62–64
HM-16	Monomer	34	40–42

3.2. Lipase-Catalyzed ROP of Cyclic Oligomers

The isolated main components of the cyclic oligomers as shown in Table 1 were subjected to the lipase-catalyzed ROP. Samples of PBS/M-6, PHS/M-6, PBS/M-16 and PHS/M-16 with various monomer ratios were prepared by the copolymerization of cyclic diol/succinate and cyclic diol/alkylthiosuccinate using CALB in bulk. A higher polymerization temperature of 120 °C was needed, because the melting point of the cyclic BS dimer was 115 °C.

Figure 1 shows a time course of molecular weight changes of the PHS/M-6 and compositional changes of the HM-6 unit in the PHS/M-6. The copolymerization was carried out for 72 h with an initial molar ratio of cyclic HS/HM-6 = 75/25 (mol/mol). The molecular weight was measured by SEC, and the HM-6 content was determined by ¹H-NMR spectroscopy. It was found that the M_w of the copolymer reached the highest value of 86000 g·mol⁻¹ after 24 h of reaction. In addition, the composition of HM-6 reached the highest of 14 mol%, although this value was lower than the feed ratio. These results indicate that cyclic diol/alkylthiosuccinate oligomers have lower polymerizability than cyclic diol/succinate oligomers due to steric hindrance from the alkyl side chain.

Figure 1. Time course of M_w (Δ) and HM-6 content (\square) of PHS/M-6 (HM-6 feed ratio: 25 mol%).



The M_w and the yield of the copolymers having various monomer ratios were obtained by the lipase-catalyzed polymerization for 24 h and the results are shown in Table 2. It was found that high molecular weight copolymers were produced. The contents of side chain units (M-6 and M-16) in all copolymers were lower than the initial feed ratio. Copolymers containing hexyl side chain units (PBS/M-6 and PHS/M-6) changed from a rigid plastic to a liquid polymer with increasing content of the alkyl side chain unit. The homopolymer with hexyl side chain units (PHM-6) was a viscous liquid below room temperature. Although copolymers containing hexadecyl side chain units (PBS/M-16 and PHS/M-16) also changed from a rigid plastic to a liquid polymer with increasing content of side chain units, the homopolymer of the hexadecyl side chain unit (PBS/M-16 and PHM-16) was a solid polymer. This indicated that the hexadecyl side chain units tended to crystallize with each other in addition to disturbing the crystallization of the main chain.

Table 2. M_w and M_w/M_n of polymers with various contents of the side chain unit.

Polymer	Feed Ratio of Side Chain Unit (mol%)	Content of Side Chain Unit in Copolymer (mol%)	M_w ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n	Yield (%)
PBS	0	0	82000	1.47	78
PBS/M-6	10	7	75000	1.54	70
	15	12	77000	1.55	72
	30	22	85000	1.61	68
	40	33	84000	1.58	65
	PBM-6	100	100	86000	1.60
PBS/M-16	7	5	64000	2.34	70
	15	11	65000	2.05	63
	25	17	63000	2.21	52
	30	23	59000	1.93	57
	PBM-16	100	100	54000	1.96
PHS	0	0	90000	1.89	75
PHS/M-6	10	6	84000	1.72	68
	25	15	88000	1.85	57
	30	17	85000	1.88	59
	33	19	95000	1.93	60
	PHM-6	100	100	87000	1.87
PHS/M-16	10	6	72000	2.24	67
	15	10	66000	1.85	57
	20	13	69000	2.31	51
	25	15	64000	2.07	54
	PHM-16	100	100	71000	2.54

3.3. Crystallinities

Crystallinities of the polymer films were measured by wide angle X-ray diffraction (WAXD). The degree of crystallinity (χ_c) was calculated using the ratio of the peak area corresponding to the crystalline structure and the total area of all peaks in the WAXD pattern. The obtained χ_c values of the copolymers are shown in Figure 2. The χ_c of the copolymer decreased with increasing content of the alkyl side chain unit. This suggests that the alkyl side chain units prevent the crystallization of the main chain, and create an amorphous area.

Figure 2 also shows that the copolymers containing butane-1,4-diol (PBS/M-6 and PBS/M-16) have higher χ_c than those of hexane-1,6-diol (PHS/M-6 and PHS/M-16). Figure 3 shows the WAXD profiles of the BS homopolymer (PBS) and HS homopolymer (PHS). The difference in profiles indicates that the crystallization processes of PBS and PHS are different. This can be explained by the ratio of ester bonds in the main chains [19]. Since PBS has a higher ratio of ester bonds, PBS can adopt a stiff crystalline structure. According to the study of Ihn *et al.*, PBS crystallizes in a monoclinic system [20]. In contrast, the crystallization process of PHS was scarcely affected by the ester bonds due to the lower ratio of the ester bonds in the main chain. The two sharp peaks detected in the WAXD patterns of PHS ($2\theta = 21^\circ$ and 24°) are similar to those of polyethylene [21]. This suggests that PHS possesses a

crystalline structure mainly consisting of a zigzag structure caused by the packing of the hexamethylene units in the main chain.

Figure 2. The degree of crystallinity (χ_c) of PBS/M-6 (\triangle), PHS/M-6 (\square), PBS/M-16 (\circ) and PHS/M-16 (∇) with various monomer contents.

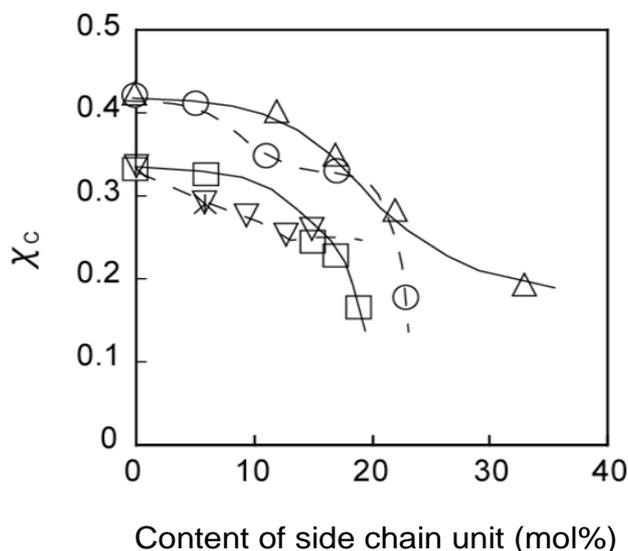
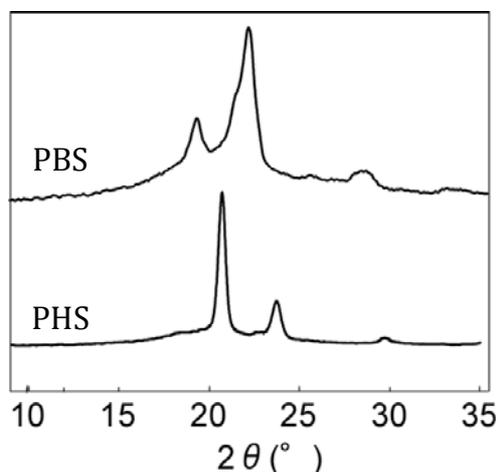
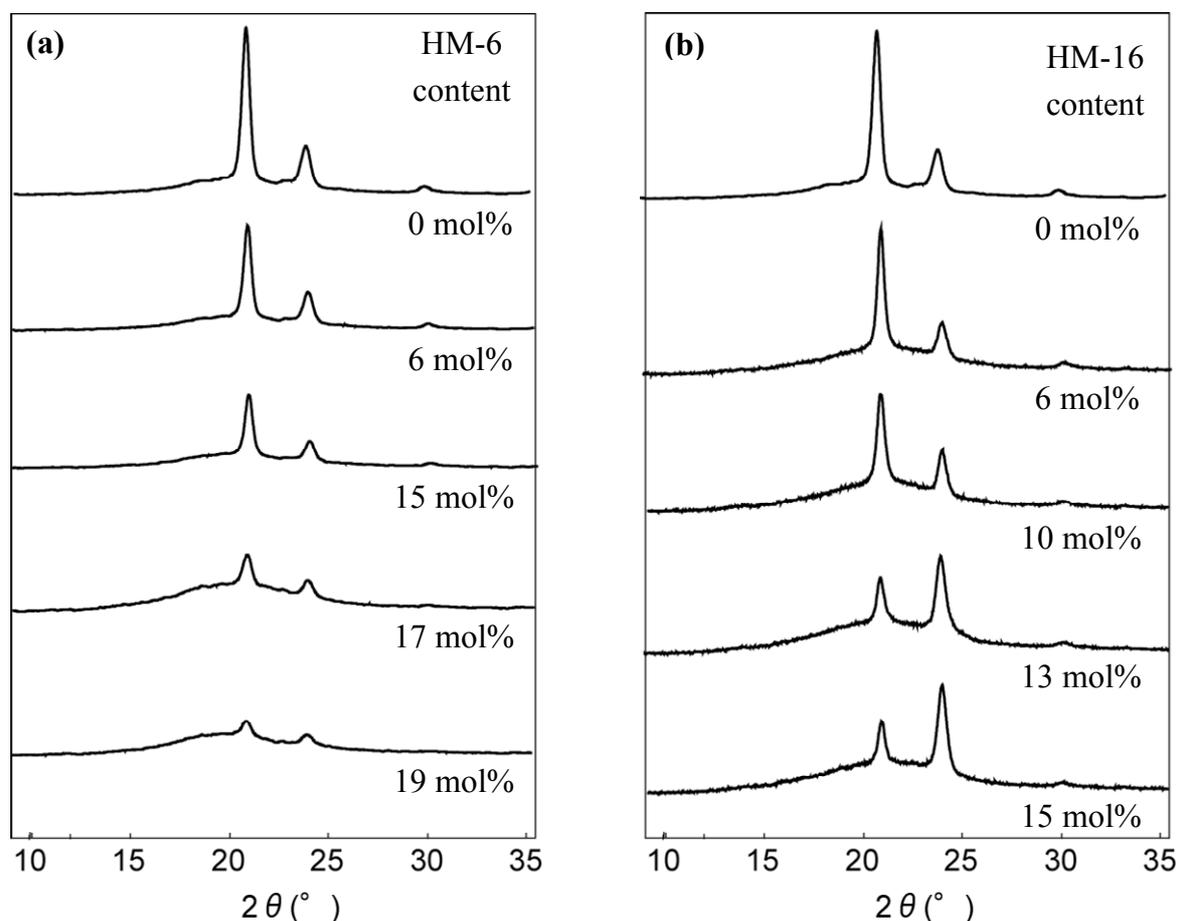


Figure 3. Wide angle X-ray diffraction spectra of PBS and PHS films.



Additionally, the alkyl side chain also affected the crystallinity of the copolymer. In order to evaluate the difference between hexyl and hexadecyl side chain units, WAXD profiles of PHS/M-6 and PHS/M-16 with various contents of side chain units are shown in Figure 4. Two crystalline peaks corresponding to methylene packing were detected around 2θ of 21° and 24° in all copolymers. Figure 4a shows that both of the crystalline peaks in PHS/M-6 decreased with increasing HM-6 content. This suggests that the hexyl side chain unit simply disturbs the crystallization process of the main chains. In contrast, Figure 4b shows that the crystalline peak at 21° in PHS/M-16 decreased with increasing HM-16 content, while the crystalline peak at 24° increased from 10 to 15 mol% with increasing HM-16 content. These results indicate that the hexadecyl side chain units create a new crystalline structure themselves, in addition to disturbing the crystallization process of the main chains.

Figure 4. Wide angle X-ray diffraction spectra of (a) PHS/M-6 and (b) PHS/M-16 films with various monomer contents.



3.4. Thermal Properties

The thermal properties of the copolymers were measured by DSC. The T_c was detected at a cooling rate of $-30\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, and the T_m was detected at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The T_g could not be obtained by DSC measurement. The results are shown in Figures 5 and 6. Both T_c and T_m of all copolymers decreased with increasing content of alkyl side chain units. This is due to the decrease in the χ_c caused by the steric hindrance of the alkyl side chain units. Also, PBS/M-6 and PBS/M-16 having higher χ_c showed higher T_c and T_m relative to PHS/M-6 and PHS/M-16.

It was found that the thermal properties of the copolymer were dependent on the alkyl side chain. Figure 7 shows the melting peaks of PHS/M-6 (a) and PHS/M-16 (b) with various contents of the alkyl side chain unit obtained by DSC measurement. Figure 7a shows that the melting peaks of PHS/M-6 broadened with the increasing content of the alkyl side chain unit, and the copolymer changes to an amorphous polymer with no melting peak. This suggests that the crystalline area of the copolymer simply decreased with increasing content of HM-6. On the other hand, new melting peaks appeared in the temperature range of $0\text{--}20\text{ }^{\circ}\text{C}$ with increasing HM-16 content above 23 mol% as shown in Figure 7b. These new peaks must correspond to the new crystalline structure created by the hexadecyl side chain units. Sharp decreases in T_m values of PBS/M-16 and PHS/M-16 as shown in Figure 6 are due to a shift of the crystalline structure from the main chains to the hexadecyl side chain units.

Figure 5. T_c of PBS/M-6 (Δ), PHS/M-6 (\square), PBS/M-16 (\circ) and PHS/M-16 (∇) with various monomer contents.

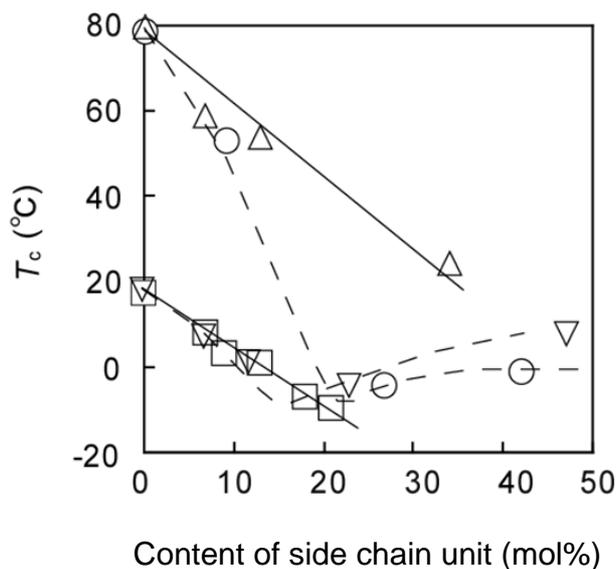


Figure 6. T_m of PBS/M-6 (Δ), PHS/M-6 (\square), PBS/M-16 (\circ) and PHS/M-16 (∇) with various monomer contents.

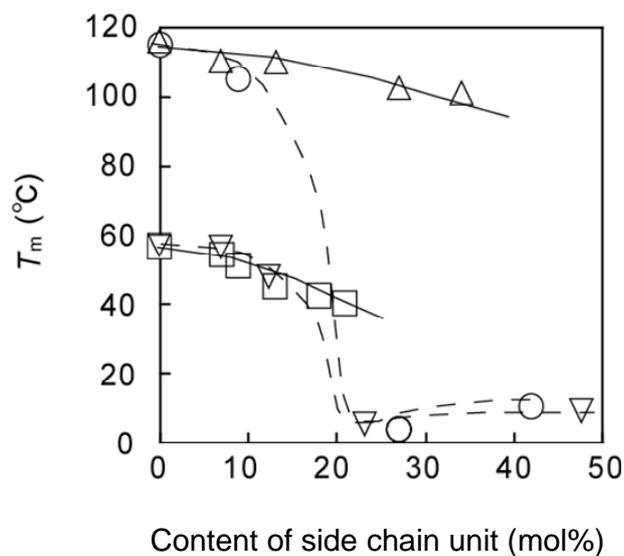
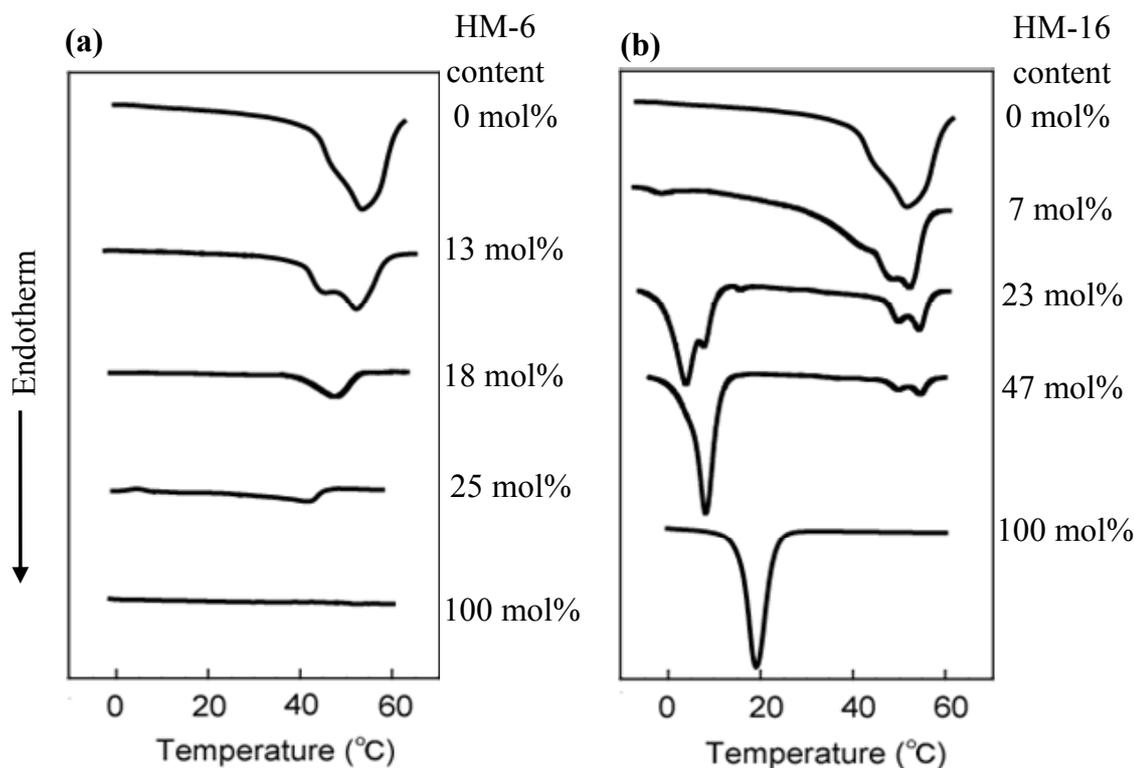


Figure 7. Melting peaks of (a) PHS/M-6 and (b) PHS/M-16 with various monomer contents.

3.5. Mechanical Properties

The mechanical properties of the copolymers were measured by tensile tests at 25 °C. Stress-strain curves of the copolymers were obtained and values of Young's modulus, tensile strength and elongation at break were calculated. As a typical example, the stress-strain curves of PHS/M-6 with various HM-6 contents are shown in Figure 8, and the values of the mechanical properties are summarized in Table 3. These properties were strongly dependent on the content of the alkyl side chain unit in the copolymer. With increasing content of the alkyl side chain unit, the Young's modulus and tensile strength simply decreased, although the elongation at break first increased and then decreased. The yield points of the copolymer disappeared with increasing content of the alkyl side chain unit as shown in Figure 8. These results indicate that a certain content of the alkyl side chain unit imparts a flexibility to the copolymer, while an excess amount of the alkyl side chain unit imparts weakness and flexibility. These tendencies were observed for all of the copolymers; thus the alkyl side chain unit was confirmed to act as a soft segment.

Cyclic stress-strain curves were obtained from cyclic loading tests with 5-cycles load-unload to the maximum elongation of 100% [22]. As a typical example, cyclic stress-strain curves of PHS/M-6 (HM-6 content: 19 mol%) are shown in Figure 9, and values of elastic recovery in the first cycle are shown in Table 3. It was found that considerable strain remains after the first cycle, and similar values of elastic recovery were obtained in subsequent cycles. The remaining strain of the copolymer may be due to the orientation of the polymer chains and the restructuring of a crystalline area with elongation. The copolymer films that underwent the elongation maintain the oriented structure of the polymer chains; therefore, further orientation is unlikely to occur in subsequent cycles. In addition, the elastic

recovery increased with increasing content of the alkyl side chain unit. It is suggested that in copolymers with lower χ_c , amorphous areas were mainly stretched, and as a result, prevented the crystalline areas from deformation [23].

Table 3. Mechanical properties of copolymers with various monomer contents.

Polymer	Content of Side Chain Unit (mol%)	Degree of Crystallinity (χ_c)	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Elastic Recovery (%)
PBS	0	0.42	292	29.8	18	–
PBS/M-6	7	0.40	195	18.9	20	–
	12	0.35	148	13.5	40	–
	22	0.28	118	12.5	485	29
	33	0.19	21.8	4.4	310	40
PBS/M-16	5	0.41	263	24.1	20	–
	11	0.35	192	22.0	25	–
	17	0.33	116	12.5	54	–
	23	0.18	12.3	2.7	10	–
PHS	0	0.33	188	16.9	392	17
PHS/M-6	6	0.32	156	15.5	594	22
	15	0.25	90.3	8.8	520	28
	17	0.23	46.3	7.6	660	39
	19	0.17	7.9	2.6	338	51
PHS/M-16	6	0.29	111	18.0	838	21
	10	0.27	57.3	10.1	582	30
	13	0.25	27.7	4.6	243	39
	15	0.26	13.5	2.6	59	–

Figure 8. Stress-strain curves of PHS/M-6 with various HM-6 contents.

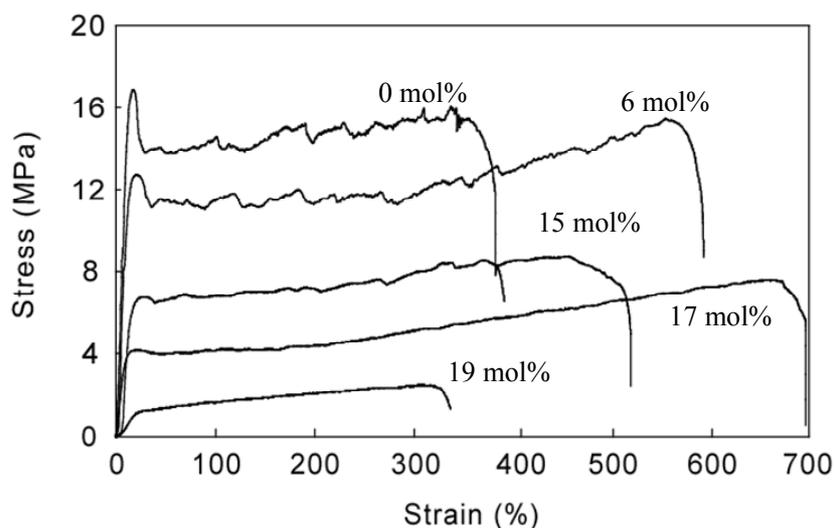
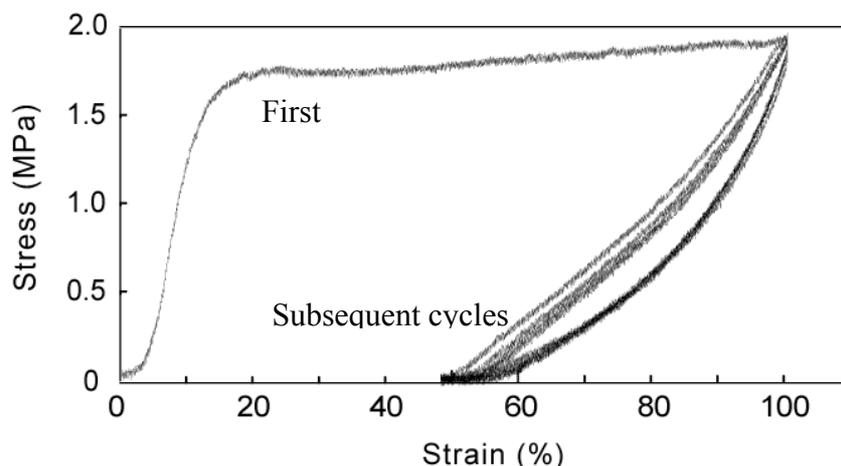
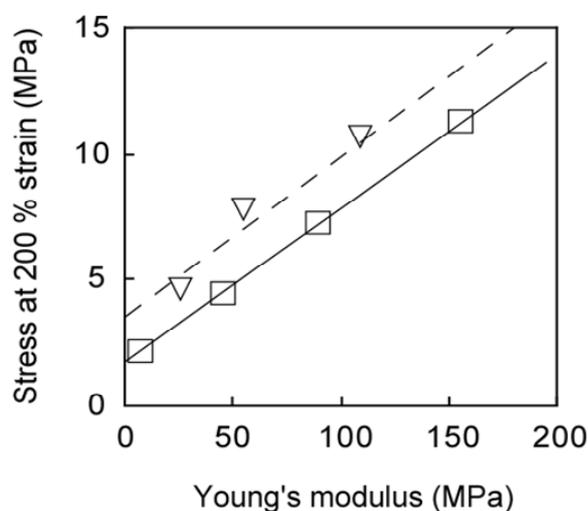


Figure 9. Cyclic stress-strain curves of PHS/M-6 (HM-6 content: 19 mol%).

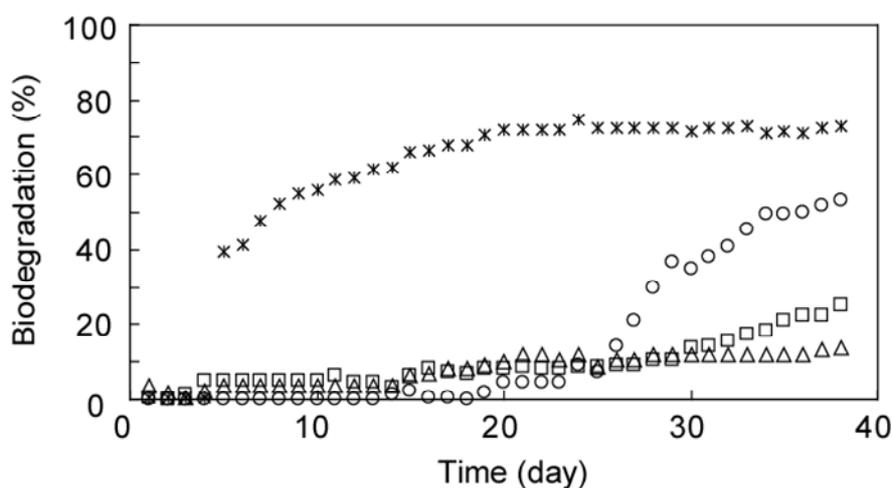
These mechanical properties were also dependent on the methylene length of both the main chain and side chain. PBS/M-6 and PBS/M-16 showed relatively higher Young's modulus and tensile strength and lower elongation at break when compared to PHS/M-6 and PHS/M-16. This indicates that the crystalline structure, which is mainly affected by the ester bonds, has rigid and inflexible properties. Additionally, PHS/M-16 showed a relatively sharper decrease in the Young's modulus and an increase in the elongation at break when compared to PHS/M-6. This is due to the extension of the alkyl side chain that leads to an increase in the steric hindrance. In contrast, the tensile strength decreased similarly between PHS/M-16 and PHS/M-6. In order to investigate this tendency, a relationship between tensile stress at 200% elongation and Young's modulus is shown in Figure 10. It was found that PHS/M-16 exhibited a higher tensile stress relative to PHS/M-6. This is due to the difference in packing effect of the alkyl side chains. Upon elongation of the copolymers, both main chains and side chains were oriented and the crystalline areas became tougher. In this case, longer alkyl side chains may produce bigger packing effects that might contribute to reinforce the crystalline area [24].

Figure 10. Relationship between Young's modulus and stress at 200% strain of PHS/M-6 (\square) and PHS/M-16 (∇) with various monomer contents.

3.6. Biodegradabilities

Biodegradabilities of PHS/M-6 with various monomer contents were evaluated using activated sludge according to the BOD tests at 25 °C for 38 days. Figure 11 shows the time course of biodegradation of PHS/M-6 as a typical example. Aniline was used as a reference for the biodegradation test. It was found that biodegradation rates of PHS/M-6 increased with increasing HM-6 content. This is due to the decrease in χ_c of PHS/M-6, as shown in Table 2. The amorphous unit increased upon increasing HM-6 content, which promoted the hydrolysis of the ester bonds in the copolymer [22].

Figure 11. BOD-biodegradation of PHS/M-6 with various HM-6 contents [0 mol% (Δ), 6 mol% (\square), 17 mol% (\circ)] and aniline (*) using activated sludge at 25 °C.



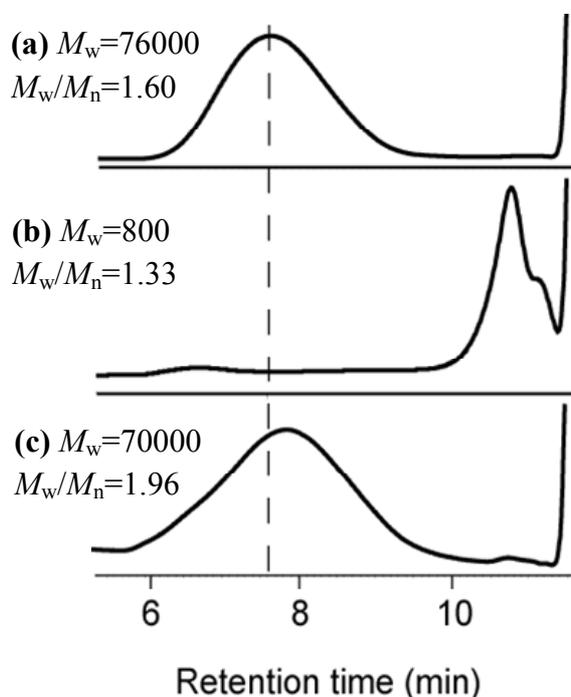
3.7. Chemical Recyclabilities

The chemical recyclabilities of the copolymers were evaluated by lipase-catalyzed degradation into cyclic oligomers and repolymerization of the resulting cyclic oligomers. Figure 12 shows SEC profile changes of PHS/M-6 (HM-6 content: 17 mol%) by the degradation and repolymerization processes. A copolymer having a M_w of 76000 $\text{g}\cdot\text{mol}^{-1}$ was completely degraded into oligomers having a M_w of 800 $\text{g}\cdot\text{mol}^{-1}$ by CALB after a 3-day reaction as shown in Figure 12a,b. No terminal carboxyl or hydroxyl groups were detected in the $^1\text{H-NMR}$ spectrum, thus confirming cyclic structures of the degradation products. Also, molecular masses corresponding to the cyclic oligomers with several ring sizes ($z = 2-8$) were observed in the MALDI-TOF MS spectrum of the degradation products, while no linear oligomers of any molecular mass could be detected. These results suggested that the degradation products exclusively consisted of the repolymerized cyclic oligomers. In order to establish a convenient method of chemical recycling, the crude product was subjected to ROP without further purification.

The lipase-catalyzed repolymerization and reprecipitation were carried out using the same method as the usual ROP. Figure 12b,c shows that the degradation products readily repolymerized to a copolymer having a M_w of 70000 $\text{g}\cdot\text{mol}^{-1}$ and HM-6 content of 16 mol%, almost the same as those of

the initial copolymer. These results confirmed the chemical recyclabilities of the copolymers by a lipase. A slight decrease in the molecular weight might be caused by a small amount of impurities.

Figure 12. (a) SEC profiles of PHS/M-6, (b) degradation products and (c) repolymerized PHS/M-6.



4. Conclusions

Novel thermoplastic elastomers, PBS/M-6, PHS/M-6, PBS/M-16 and PHS/M-16, were prepared by the lipase-catalyzed polymerization of bio-based diols and dicarboxylic acids via cyclic oligomers. These copolymers exhibited biodegradability, chemical recyclability and a wide range of mechanical properties such as Young's modulus of 8–292 MPa, tensile strength of 2.6–29.8 MPa and elongation at break of 10–838%. These values were dependent on the content of alkyl side chain units and the methylene units in both the main and side chains. Based on these results, these novel polyesters have potential for applications as environmentally benign thermoplastic elastomers in the field of polymeric materials.

Acknowledgments

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