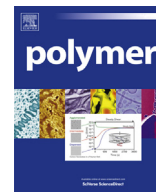




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Conformational characteristics and configurational properties of poly(ethylene succinate) and poly(butylene succinate) and structure–property–function relationships of representative biodegradable polyesters

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ABSTRACT

Conformational characteristics and configurational properties of synthetic biodegradable polyesters, poly(ethylene succinate) and poly(butylene succinate), have been investigated by NMR experiments and molecular orbital calculations on their model compounds and the rotational isomeric state calculations for the two aliphatic polyesters. The results have been related to their crystal structures and thermal properties and compared with those obtained previously for poly((*R*)-3-hydroxybutyrate) and poly(lactic acid) to elucidate structure–property relationships of the representative biodegradable polyesters. In addition, selective affinities to degradative enzymes of the four polyesters have been satisfactorily explained in terms of their conformational characteristics and interactions with the depolymerases.

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1. Introduction

Biodegradable polyesters may be classified into three types: natural, semi-natural, and synthetic polyesters. Poly((*R*)-3-hydroxybutyrate) (PHB) is a purely natural polyester, because it is synthesized and decomposed by microorganisms [1]. Poly(lactic acid) (PLA) is artificially produced from carbon-neutral lactic acid or lactide [2]. Poly(ethylene succinate) (PES, Fig. 1b) and poly(butylene succinate) (PBS, Fig. 1d) are produced from petrochemicals such as succinic acid, dimethyl succinate, ethylene glycol, and 1,4-butanediol [3,4]. These chemicals will be derived from carbon-neutral resources in the future.

In previous studies [5,6], we investigated conformational characteristics and configurational properties of PHB and PLA and elucidated their solution properties, crystal structures, crystallization behaviors, and interactions with degradative enzymes. This study has dealt with PES and PBS: Conformational preferences of the skeletal bonds have been revealed through NMR experiments and molecular orbital (MO) calculations on their small model compounds and related to crystal structures of the two polyesters. Conformational free energies, evaluated from the MO calculations

and established through comparison with the NMR experiments, were applied to the refined rotational isomeric state (RIS) scheme [7–9] to derive configurational properties and thermodynamic quantities of PES and PBS, compare them with those of PHB and PLA, and clarify differences between the four biodegradable polyesters. As will be stated below, it is known that these polyesters are selectively degraded by specific microorganisms and enzymes. The selectivity is also treated herein to be explained in terms of the conformational characteristics of the polyesters.

Tokawa et al. [1,10–14] have investigated biodegradation behaviors of various polyesters including PHB, PLA, PES, and PBS under different conditions with a number of microorganisms and purified degradative enzymes to find the following facts: (1) The populations of polymer-degrading microorganisms can be estimated to be in the order of PHB > PBS > PLA. (2) In the natural environment, PHB-degraders are widely distributed among families of *Pseudonocardiaceae* and related genera, *Micromonosporaceae*, *Thermonosporaceae*, *Streptosporangiaceae*, and *Streptomycetaceae*. (3) Lipases hydrolyze aliphatic polyesters with relatively many methylene groups, e.g., poly(ϵ -caprolactone), poly(ester carbonate), PES, and PBS but are incapable of degrading optically active polyesters such as PHB and PLA. (4) A serine protease, proteinase K, which selectively cleaves the Ala–Ala linkage of

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silk fibroins, can also effectively degrade PLA. This may be partly because of the similarity in chemical structure between alanine and lactic acid. (5) The melting point of the polyesters is closely related to the enzymatic degradability.

This study has also aimed to interpret the above microbiological findings in terms of polymer physicochemistry.

2. Methods

2.1. Sample preparation

Commercial available chemicals were used as received: ethylene glycol, 1,4-butanediol, acetyl chloride, diethyl ether, 1,4-dioxane, ethyl acetate, *n*-hexane, silica gel (Wako Pure Chemical Industries, Tokyo, Japan); succinyl chloride, acetyl chloride-¹³C (Sigma–Aldrich Japan, Tokyo, Japan).

All syntheses here employed the following experimental setup: a four-necked flask (under a stream of dry nitrogen) equipped with a mechanical or a magnetic stirrer and a Dimroth condenser connected to a calcium chloride drying tube. In silica gel column chromatography, a mixed eluting solvent (ethyl acetate:*n*-hexane = 1:1) was used. All products were identified by NMR.

2.1.1. Dimethyl succinate (DMS)

Methanol (2.7 mL, 67 mmol) was added to succinyl chloride (3.0 mL, 27 mmol) and stirred for 1 h. After methanol (1.0 mL, 25 mmol) was superadded, the mixture was gradually heated up to 70 °C, kept there for 1 h to remove generated hydrogen chloride, and then cooled down to ambient temperature. After pyridine (1.1 mL, 14 mmol) was added, the reaction mixture was stirred, filtrated, and condensed on a rotary evaporator to yield DMS.

2.1.2. Ethylene glycol diacetate (EGDA)

Acetyl chloride (4.5 mL, 63 mmol) was added to ethylene glycol (1.97 g, 32 mmol) and pyridine (5.03 g, 64 mmol) stirred in the four-necked flask, and then the mixture was stirred for 3 h with the flask bathed in ice water. Diethyl ether was added into the flask, and the mixture was filtrated to remove white precipitate. The filtrate was subjected to the silica gel column chromatography (R_f of the product ~ 0.6) and condensed to yield EGDA (yield 32%).

2.1.3. Ethylene glycol diacetate-¹³C (EGDA-¹³C)

Acetyl chloride (30 mL, 0.42 mol) was added to ethylene glycol (31.4 g, 0.51 mol) dissolved in 1,4-dioxane (52 mL, 0.61 mol) stirred in the four-necked flask. The mixture was refluxed for 2 h with the flask heated at 120 °C in an oil bath [15]. After cooled down to ambient temperature, the reaction mixture was condensed and purified by the column chromatography (R_f of the product ~ 0.3) to yield ethylene glycol monoacetate (yield 42%).

Acetyl chloride-¹³C (0.25 g, 3.1 mmol) was added to a mixture of ethylene glycol monoacetate (0.43 g, 4.1 mmol) and pyridine (0.32 g, 4.1 mmol) and stirred for 3 h. The handling described in Section 2.1.2 was employed to yield EGDA-¹³C (56%).

2.1.4. Ethylene glycol di(methyl succinate) (EGDMS)

This compound was prepared according to van der Brand et al. [16].

2.1.5. Butylene glycol diacetate (BGDA)

Acetyl chloride (5.0 mL, 70 mmol) was added to 1,4-butanediol (3.8 g, 42 mol) and pyridine (6.7 g, 85 mmol) in the flask kept at 0 °C, and then the mixture was stirred at 0 °C for 3 h. Diethyl ether was added into the flask, and yellow solid was precipitated and

removed by filtration. The filtrate (2 mL) underwent extraction with ethyl acetate (100 mL) and water (100 mL), and this extraction was repeated four times. The organic layer was condensed and subjected to the column chromatography (R_f of the product ~ 0.6, yield 26%).

2.1.6. Butylene glycol diacetate-¹³C (BGDA-¹³C)

Acetyl chloride (5.0 mL, 70 mmol), 1,4-butanediol (7.6 g, 84 mmol), and pyridine (6.7 g, 85 mmol) were treated in the same manner as described in Section 2.1.5 to yield butylene glycol monoacetate (R_f of the product ~ 0.3, yield 25%).

Acetyl chloride-¹³C (0.25 g, 3.1 mmol) was added to butylene glycol monoacetate (0.51 g, 3.9 mmol) and pyridine (0.30 g, 3.8 mmol), and the mixture was stirred at 0 °C for 3 h and purified as described in Section 2.1.2 to yield BGDA-¹³C (64%).

2.2. NMR measurements

¹H (¹³C) NMR spectra were recorded at 500 MHz (125.7 MHz) on a JEOL JNM-ECA500 spectrometer equipped with a variable temperature controller in the Center for Analytical Instrumentation of Chiba University. The measurement temperatures were 15, 25, 35, 45, and 55 °C and maintained within ±0.1 °C fluctuations. Free induction decays (FIDs) were accumulated 32 (256) times. The $\pi/2$ pulse width, data acquisition time, and recycle delay were 5.6 (5.0) μ s, 3.3 (2.0) s, and 3.7 (2.0) s, respectively. In the ¹³C NMR experiments, the gated decoupling technique was employed under the conditions given in the above parentheses. The solvents were cyclohexane-*d*₁₂ (C₂D₁₂), benzene-*d*₆ (C₆D₆), chloroform-*d* (CDCl₃), methanol-*d*₄ (CD₃OD), and dimethyl-*d*₆ sulfoxide ((CD₃)₂SO), and the solute concentration was approximately 5 vol%. The NMR spectra were simulated with the gNMR program [17] to yield chemical shifts and coupling constants.

2.3. MO calculations on model compounds

Density functional and *ab initio* MO calculations were carried out with the Gaussian09 program [18] installed on an HPC Systems 5000-Z800 computer. For each conformer of model compounds, the geometrical parameters were fully optimized at the B3LYP/6-311+G(2d,p) level, and the thermal-correction term to the Gibbs free energy (at 25 °C) was calculated at the same level. Bond lengths, bond angles, and dihedral angles used in the refined RIS computations were chosen from the optimized geometrical parameters (see Tables S4 and S5, Supplementary data). All the self-consistent field calculations were conducted under the tight convergence. With the optimized geometry, the electronic energy was computed at the MP2/6-311+G(2d,p) and M062X/6-311+G(2d,p) level [19]. The Gibbs free energy was evaluated from the electronic energy and the thermal-correction term, being given here as the difference from that of the all-trans conformer and denoted as ΔG . Vicinal ¹H–¹H and ¹³C–¹H coupling constants used to determine bond conformations of model compounds were calculated at the B3LYP/6-311+G(3df,3pd) level [20]. The ΔG values of the model compounds in benzene and chloroform at 25 °C were also calculated at the MP2/6-311+G(2d,p) and M062X/6-311+G(2d,p) level with the integral equation formalism of the polarizable continuum model [21].

Herein the dihedral angle is defined according to the tradition in polymer science [7]: trans (t) ~±0°, cis (c) ~±180°, gauche⁺ (g⁺) ~+120°, and gauche⁻ (g⁻) ~-120°. The dihedral angle (ϕ) can be converted to that (Φ) recommended by IUPAC [22] according to $\Phi = -\text{sign}(\phi)(180 - |\phi|)$, where the function, $\text{sign}(\phi)$, returns the sign of ϕ , and *vice versa*: $\phi = -\text{sign}(\Phi)(180 - |\Phi|)$. Non-SI units are

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