Biodegradable Polymers Based on Renewable Resources: Polyesters Composed of 1,4 : 3,6-Dianhydrohexitol and Aliphatic Dicarboxylic Acid Units

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SYNOPSIS

A series of polyesters was synthesized by the bulk polycondensations of the respective combinations of three stereoisomeric 1,4 : 3,6-dianhydrohexitols [1,4 : 3,6-dianhydro-D-glucitol (**1**), 1,4 : 3,6-dianhydro-D-mannitol (**2**), and 1,4 : 3,6-dianhydro-L-iditol (**3**)] with succinyl dichloride (**4a**), glutaryl dichloride (**4b**), adipoyl dichloride (**4c**), and sebacoyl dichloride (**4d**). Biodegradability of these polyesters was investigated by three different methods, i.e., degradation in an activated sludge, soil burial degradation, and enzymatic degradation. Although polyesters (**7b–7d**) based on **3** and polyester **6a** derived from **2** and **4a** were crystalline and scarcely biodegraded, all the other amorphous polyesters were more or less biodegradable. Biodegradability of the polyesters was found to vary significantly depending on their molecular structures. Soil burial degradation of polyesters in the soil that was treated with antibiotics, together with electron scanning microscopic observation, showed that polyesters **5b** and **5c** prepared from **1** and **4b** or **4c** were degraded by both bacteria and filamentous fungi, whereas polyester **5d** from **1** and **4d** was degraded primarily by filamentous fungi. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Development of biodegradable polymers is one of the most important and urgent subjects from a standpoint of environmental preservation on the earth. Over decades, great efforts have been made to develop practically applicable, biodegradable polymers,[1-6] and, in fact, some of them have been commercialized. However, except for several biodegradable polymers based on naturally occurring polysaccharides, commercially available biodegradable polymers are mostly aliphatic polyesters as represented by poly(3-hydroxyalkanoate)s, poly(ε-caprolactone), poly(butylene succinate), and so on. Although these polyesters including their copolyesters can cover over a broad range of properties needed for most purposes, specific requirements for polymeric materials vary so widely that it is desirable to develop different types of biodegradable polymers with physical and chemical properties differing from those of conventional aliphatic polyesters.

Effective utilization of renewable biomass resources as raw materials for biodegradable polymers is an attractive and challenging target of investigation. Recently, we reported the synthesis of polyesters based on 1,4 : 3,6-dianhydro-D-glucose (**1**) and 1,4 : 3,6-dianhydro-D-mannitol (**2**), which are readily prepared from D-glucose and D-mannose, respectively.[7,8] These diols can be used as bifunctional monomers suitable for synthesizing polyesters by polycondensation[9,10] and polyurethanes by polyaddition.[11-13] Preliminary degradation tests on the polyesters derived from the 1,4 : 3,6-dianhydrohexitols and aliphatic dicarboxylic acids showed that most of the polyesters underwent spontaneous hydrolysis in a phosphate buffer solution of pH 7.4 at 50°C, whereas they were reluctant to be hydrolyzed at 27°C. These polyesters were more or less degraded at 27°C by treatment with an activated sludge or by prolonged burial in composted soil.[7] These findings

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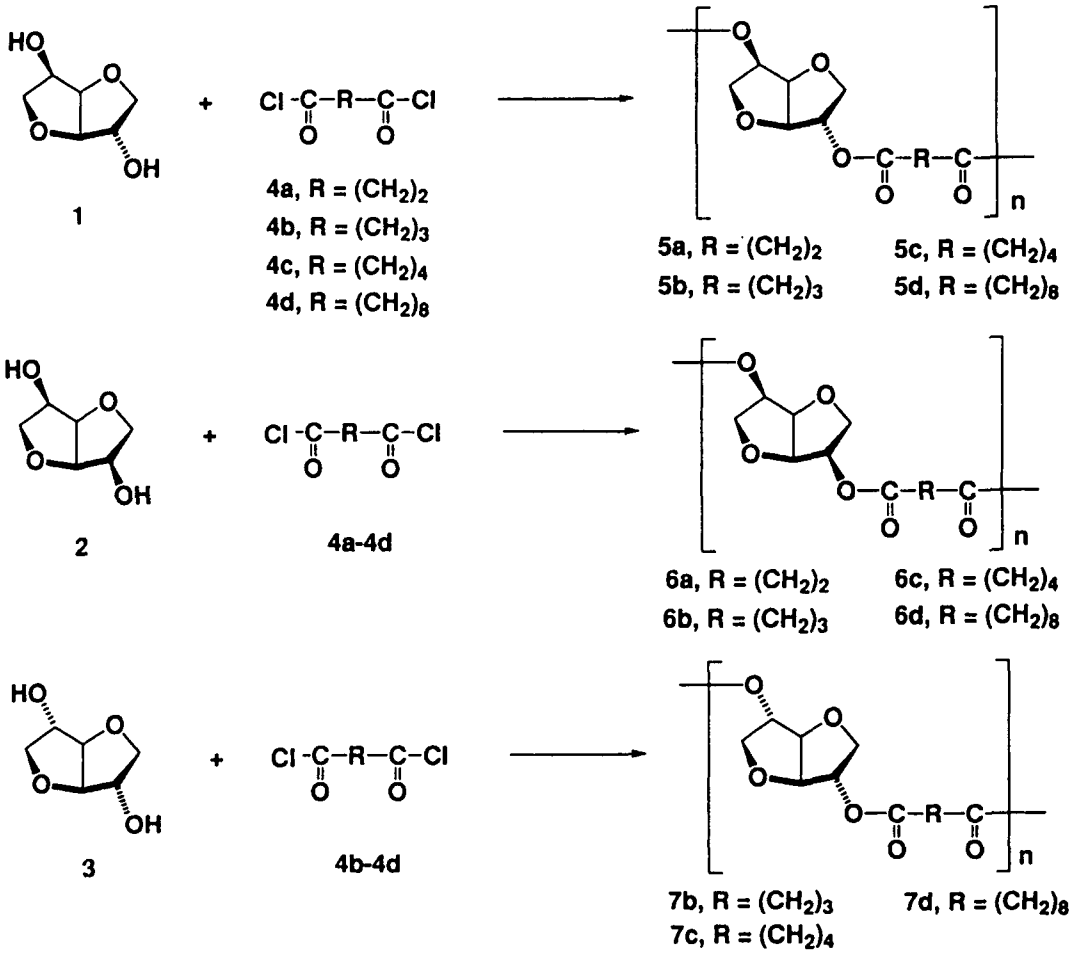
Journal of Applied Polymer Science, Vol. 62, 2257–2265 (1996)
 CCC 0021-8995/96/132257-09

stimulated us to investigate the biodegradability of the polyesters containing 1,4 : 3,6-dianhydrohexitol units along the polymer chains. The present article deals with further investigation on the biodegradability of a series of 11 different polyesters derived from three stereoisomeric 1,4 : 3,6-dianhydrohexitols including 1,4 : 3,6-dianhydro-L-iditol (**3**) and four different aliphatic dicarboxylic acids (**4a–4d**):



EXPERIMENTAL

Materials

Commercially available 1,4 : 3,6-dianhydro-D-glucitol (**1**) and 1,4 : 3,6-dianhydro-D-mannitol (**2**) were purified by repeated recrystallization from chloroform for **1** and from chloroforom-hexane (2 : 1, v/v) for **2**. 1,4 : 3,6-Dianhydro-L-iditol (**3**) was prepared from **2** via the Mitsunobu reaction[14] with benzoic acid in the presence of diethyl azodicarboxylate and triphenylphoshine.[15] The diol was recrystallized from a mixed solvent of *n*-hexane and ethyl acetate (3 : 1, v/v). Succinyl dichloride (**4a**), glutaryl dichloride (**4b**), adipoyl dichloride (**4c**), and sebacoyl dichloride (**4d**) were prepared by the reactions of the corresponding dicarboxylic acids with thionyl chloride using a small amount of *N,N*-dimethylformamide as a promoter. These dichlorides were purified by distillation under nitrogen.

Polycondensation

Polycondensation was carried out in bulk at 160°C, first at normal pressure for 6 h, then under reduced pressure (ca. 40 mmHg) by an aspirator for 2 h, and finally under vacuum (1 mmHg) for 12 h. The polymers were purified by repeated reprecipitation using chloroform and methanol as a pair of solvent and precipitant. They were dried under reduced pressure to a constant weight.

Characterization

Molecular weights of polyesters were estimated by size-exclusion chromatography (SEC) using chloroform as an eluent and standard polystyrene as a reference. Surfaces of polyester films after soil burial tests were observed by JEOL JSM-F7 and Hitachi S-2150 scanning electron microscopes. Microscope surface reflectance FTIR spectra of polyester films were taken by a DIGILAB FTS-60 spectometer with a DIGILAB UMA-300A IR microscope. Glass transition temperatures and melting points of polyesters were determined by a Perkin-Elmer DSC-2 differential scanning calorimeter or a Seiko-Electronics DSC100 differential scanning calorimeter. Total organic carbon contents in aqueous solutions produced by enzymatic degradation of the polyesters were analyzed by a Shimadzu TOC-500 instrument. Tensile properties of the polyester films (thickness, 0.3 mm) were measured by a Toyo Measuring Instrum Tensilon/UTM-4LH.

Degradation in Activated Sludge

A sample of the polyester (25 mg) was taken in each of several test tubes with an inner diameter of 22 mm. A small amount of dichloromethane was added to dissolve the sample. By rotating the test tube and slowly evaporating the solvent, the bottom part (height from the bottom, about 1.5 cm) of the inner wall of the test tube was coated with a thin film of the polyester. An activated sludge solution (50 mL) taken from a sewage treatment plant in Meito-ku, Nagoya, was added to the test tube, and air was constantly bubbled into the activated sludge at 27°C. After a designated time, the mixture of the activated sludge and polyester sample was filtered, washed with water, and dried. The polyester residue was extracted with chloroform and separated from the activated sludge by filtration. The polyester residue was recovered by the evaporation of the filtrate. After it was thoroughly dried, its weight and molecular weight were measured.

Soil Burial Degradation

A soil burial degradation test was undertaken on thin films (10 × 25 mm, thickness, 140 μm) or disks (diameter, 10 mm, thickness 0.5 mm). The films or disks were buried in soil in a desiccator, in which the relative humidity was adjusted to 70–80% by a saturated solution of ammonium nitrate. The soil, which had been composted for more than 10 years, was obtained from the Nagoya University farm. The desiccator was placed in a room thermostated at 27°C. After designated times, the films or disks were taken out, washed with water, and dried. When the soil was adhered to the samples and could not be removed by washing, the samples were extracted with chloroform, and the soil was separated by filtration. After the evaporation of the solvent from the filtrate, the residue was dried to a constant weight under reduced pressure. The weights and molecular weights of the recovered polyesters were determined.

Enzymatic Degradation

A powdery sample or finely pulverized sample (25 mg) after freeze-drying from a 1,4-dioxane solution was placed in each test tube with a cap, to which a phosphate buffer solution of pH 7.0 (10 mL) and *Rhizopus delemar* lipase (250 units) were added. The test tubes were incubated with constant shaking with 80 strokes per minute for 24 h at 37°C. As blank tests, test tubes containing only either the sample or the enzyme were shaken under the same conditions. Ten drops of 1*N* hydrochloric acid was added to each mixture and the total organic carbon content dissolved in the buffer was determined.

RESULTS AND DISCUSSION

Preparation and Properties of Polyesters

Eleven different polyesters were prepared by bulk polycondensations of the combinations of the three stereoisomeric 1,4 : 3,6-dianhydrohexitols (**1–3**) and four different aliphatic dicarboxylic acid dichlorides (**4a–4d**) at 160°C. Some of the typical polymerization data are presented in Table I.

According to X-ray diffraction measurements, polyesters **7b–7d** based on 1,4 : 3,6-dianhydro-L-iditol (**3**) and polyester **6a** derived from 1,4 : 3,6-dianhydro-D-mannitol (**2**) and succinyl dichloride (**4a**) were crystalline, whereas the other polyesters were amorphous. Thermal transition temperatures and solubility of these polyesters are summarized in Table II. The solubility of polyesters increases with increasing methylene lengths of the diacid components for the series of polyesters based on dianhydroglucitol **1** and dianhydromannitol **2.** Particularly, polyesters **5d** and **6d** containing sebacoyl units dissolved even in benzene and toluene. In contrast, the solubility of polyesters based on dianhydroiditol **3** is much lower because of their crystallinity.

Some of the polyesters were solvent-cast into thin films, and their tensile properties were measured.

Table I Synthesis of Polyesters by Polycondensations of 1,4 : 3,6-Dianhydrohexitols (1–3) with Aliphatic Dicarboxylic Acid Chlorides (4a–4d)

Diol	Diacid Chloride	Temperature (°C)	Time (h)	Polyester	Yield (%)	M_n[a] × 10^{-3}	$\frac{M_w}{M_n}$[a]
1	**4a**	160	20[b]	**5a**	97	8	1.8
1	**4b**	160	20[b]	**5b**	93	20	1.7
1	**4c**	160	20[b]	**5c**	92	26	1.5
1	**4d**	160	20[b]	**5d**	88	34	1.2
2	**4a**	160	10[c]	**6a**	91	9	1.8
2	**4b**	160	10[c]	**6b**	98	11	1.6
2	**4c**	160	20[b]	**6c**	95	20	1.5
2	**4d**	160	20[b]	**6d**	80	18	1.4
3	**4b**	160	20[b]	**7b**	97	18	1.7
3	**4c**	160	20[b]	**7c**	93	34	1.3
3	**4d**	160	20[b]	**7d**	95	28	1.4

In bulk; equimolar diol and diacid chloride (7.85–39.5 mmol) were charged.
[a] By SEC (solvent, chloroform; polystyrene standard).
[b] 6 h/760 mmHg, 2 h/20 mmHg, 12 h/1 mmHg.
[c] 6 h/760 mmHg, 2 h/20 mmHg, 2 h/1 mmHg.

The tensile properties varied markedly on the structures of the polyesters. For example, the Young's modulus, tensile strength, and elongation at break were 13.2 MPa, 4.0 MPa, and 1890% for polyester **5d** and 408 MPa, 13.7 MPa, and 19% for polyester **7c**, respectively.

Degradation in Activated Sludge

Degradation tests on the two series of polyesters based on 1,4 : 3,6-dianhydro-D-glucitol (**1**) and 1,4 : 3,6-dianhydro-D-mannitol (**2**) were carried out in an activated sludge at 27°C. The changes in the recovery of the water-insoluble polymer with immersion time in the activated sludge for polyesters **5a–5d** and polyesters **6a–6d** are shown in Figures 1 and 2, respectively.

In comparison with the spontaneous hydrolysis in the phosphate buffer solution (broken line; hydrolysis for **5a** in Fig. 1 and for **6b** in Fig. 2), most of the polyesters were more easily degraded in the activated sludge. These results strongly suggest that

Table II Thermal Transition Temperatures and Solubilities of Polyesters Derived from 1,4 : 3,6-Dianhydrohexitols (1–3) and Aliphatic Dicarboxylic Acid Chlorides (4a–4d)

	Polyesters										
	5a	**5b**	**5c**	**5d**	**6a**	**6b**	**6c**	**6d**	**7b**	**7c**	**7d**
T_g[a] (°C)	36	28	40	−10	75	37	28	−8	50	45	0
T_m[a] (°C)	—	—	—	—	175	—	—	—	181	164	134
Solubility[b]											
Toluene	●	●	●	○	●	●	●	○	●	●	◑
THF	●	○	○	○	●	◑	○	○	●	●	◑
Chloroform	○	○	○	○	○	○	○	○	○	○	○
m-Cresol	○	○	○	○	○	○	○	○	○	○	○
Acetonitrile	○	○	○	○	●	◑	○	○	●	●	●
Methanol	●	●	●	●	●	●	●	●	●	●	●
Me_2SO	○	○	○	○	●	○	○	○	◑	●	●
Water	●	●	●	●	●	●	●	●	●	●	●

[a] By DSC.
[b] At room temperature; 1 mg/mL; ○, soluble; ◑, partially soluble; ●, insoluble.

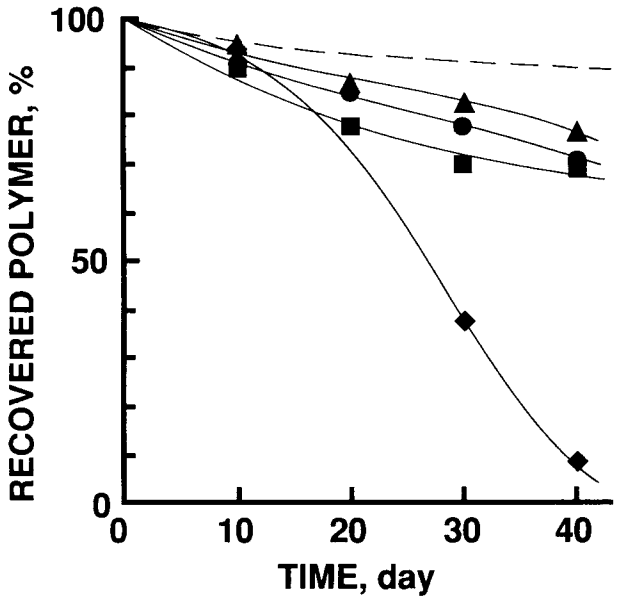


Figure 1 Recovery (wt %) of water-insoluble polymer in the degradation of polyesters **5a–5d** in an activated sludge. Temp, 27°C; pH 7.4. (■) **5a**; (●) **5b**; (▲) **5c**; (♦) **5d**.

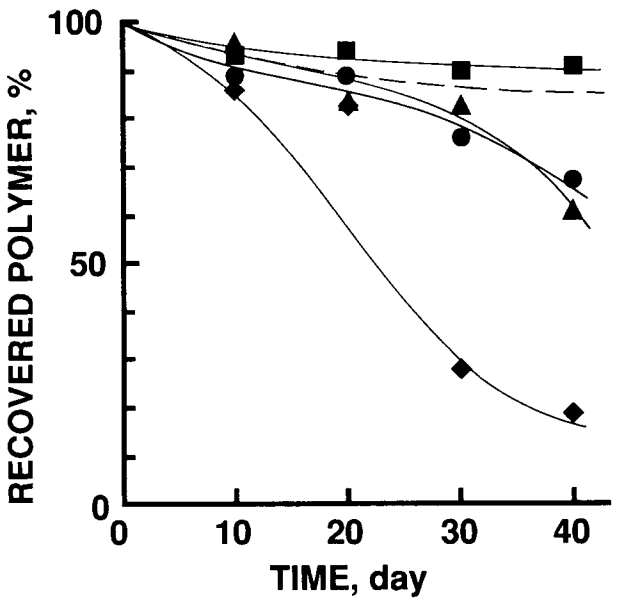


Figure 2 Recovery (wt %) of water-insoluble polymer in the degradation of polyesters **6a–6d** in an activated sludge. Temp, 27°C; pH 7.4. (■) **6a**; (●) **6b**; (▲) **6c**; (♦) **6d**.

these polyesters are more or less biodegraded in the activated sludge, although hydrolytic degradation takes place to some extent. In this connection, it is to be noted here that both diols **1** and **2** were found to be catabolized in an active sludge to yield carbon dioxide and water.[7] Polyesters **5d** and **6d** containing sebacoyl units were degraded particularly rapidly. These findings are in accordance with the enzymatic degradability of the polyesters which will be described later.

Soil Burial Degradation

Figure 3 shows the changes in the weight % of the recovered polyester disks with time in the soil burial test. Polyesters **5d** and **6d** containing sebacoyl units were almost completely degraded in 1 month. Polyesters **5c** and **6c** containing adipoyl units were also relatively rapidly degraded, the recovery of the polymers being only 7% for **5c** and 38% for **6c** after the soil burial for 3 months. Polyester **6b** containing glutaryl units was degraded nearly completely in 6 months, whereas polyesters **5a** and **5b** were degraded to a lesser extent in the same period. Crystalline polyesters **6a** and **7b–7d** were hardly degraded in the soil burial test.

Figure 4 demonstrates the change in the molecular weight distribution of polyester **5b** with soil burial time. The peak top of the SEC curve of the sample after soil burial for 4 months only slightly shifted to lower molecular weight. The shape of the SEC curve after soil burial for 6 months became

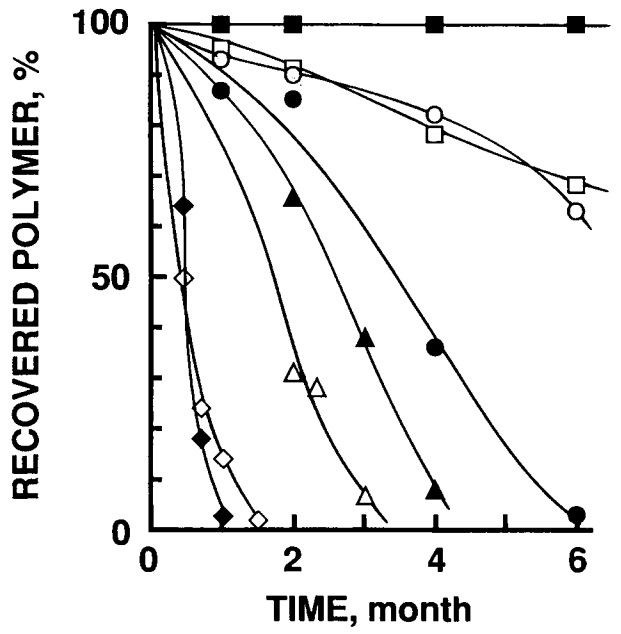


Figure 3 Changes in the recovery (wt %) of polyester disks with soil burial time: composted soil; pH 6.8; temp, 27°C; humidity 70–80%; disk thickness 0.5 mm. (□) **5a**; (○) **5b**; (△) **5c**; (◇) **5d**. (■) **6a**; (●) **6b**; (▲) **6c**; (♦) **6d**.

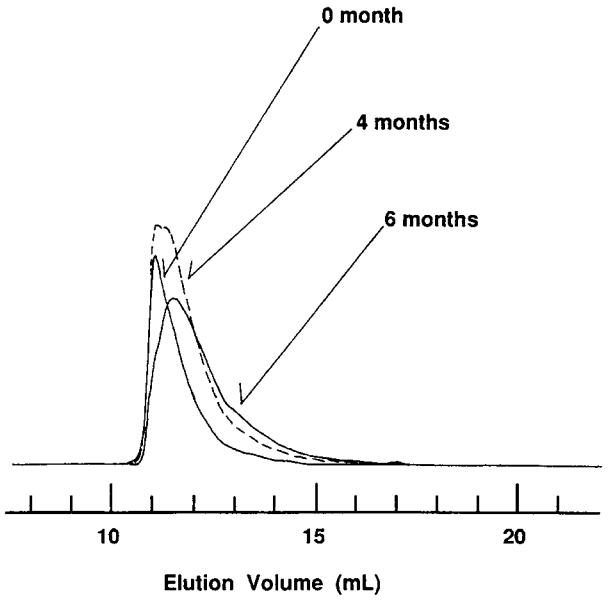


Figure 4 SEC profiles of polyester **5b** before and after soil burial test. Composted soil; disk thickness, 0.5 mm.

considerably different from the original curve and the polydispersity index increased from 1.7 to 2.1.

The soil used for the test had been composted for more than 10 years and was slightly acidic (pH 6.6–6.8). Therefore, hydrolysis might have been responsible for the degradation. To check this point, hydrolysis of polyesters **5c** and **6c** was undertaken in a phosphate buffer solution of pH 6.6 at 27°C. The recovery after immersion of the disks of these polyesters in the buffer for 3 months was 99% for **5c** and 98% for **6c**, indicating that these polyesters were scarcely hydrolyzed in the buffer solution of pH 6.6. Therefore, the findings that the polyester disks were nearly completely degraded in the soil burial test strongly suggest that these polyesters were biodegraded in the soil. In fact, electron scanning micrography shows that the surface of the disks were eroded by bacteria and fungi.

Polyesters **5c** and **5d** were solvent-cast into films and they were buried in the soil. The transparent films of polyester **5c** became opaque and were eroded significantly after 30 days, and their original shape was completely lost after 40 days (Fig. 5). Films of polyester **5d** were more rapidly degraded than were the films of polyester **5c**.

Microscope FTIR surface reflectance spectra of a film of polyester **5c** before and after the soil burial test (A and B) and the difference spectrum between them (C) are shown in Figure 6. The difference spectrum clearly shows peaks at 3300 (ν_{N-H}), 1655 ($\nu_{C=O}$), and 1545 (δ_{N-H}) cm^{-1}, which are probably due to peptide linkages of some microorganisms adhered to the surface of the film.

An eroded film of polyester **5c** after the soil burial test was dyed with a solution of cotton blue–lactophenol, and the dyed film was observed by an optical microscope. The film was dyed blue here and there, in particular, in the vicinity of the periphery of the holes. The blue color was supposed to be developed by the reactions of cotton blue with sugar moieties on the cell walls of microorganisms. Since the blue parts were fibrous, it appears that the microorganisms on the surface of the film were mostly filamentous fungi.

Figure 7 shows a scanning electron micrograph of polyester **5c** after soil burial for 10 days. It is clearly seen that the surface of the films is significantly eroded by both filamentous fungi and bacteria. In contrast, only filamentous fungi were observed on the surface of a film of polyester **5d** after the soil burial.

To determine whether either filamentous fungi or bacteria, or both, are responsible for the soil burial degradation of these polyesters, additional soil burial degradation tests were undertaken in the soil that was treated by different types of antibiotics, i.e., in soil (B) to which streptomycin (1 mg/g), an antibacterium, was added, and in the soil (C) to which cycloheximide (0.1 mg/g), an antifungus, was added.

As the photograph in Figure 8 demonstrates, in the untreated soil (A), the films of polyesters **5b, 5c,** and **5d** were more or less degraded during the soil burial for 30 days. In the streptomycin-treated soil (B) in which filamentous fungi were supposed to be active, all the films of the polyesters were

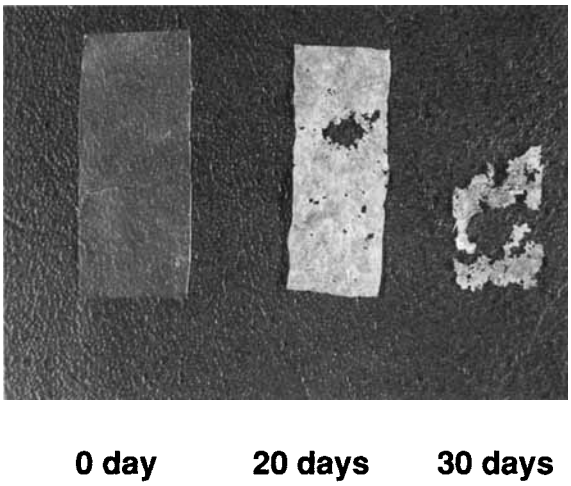


Figure 5 Photograph of polyester films **5c** before and after soil burial test. Composted soil; pH 6.8; temp, 27°C; humidity, 70–80%; film thickness 140 μm.

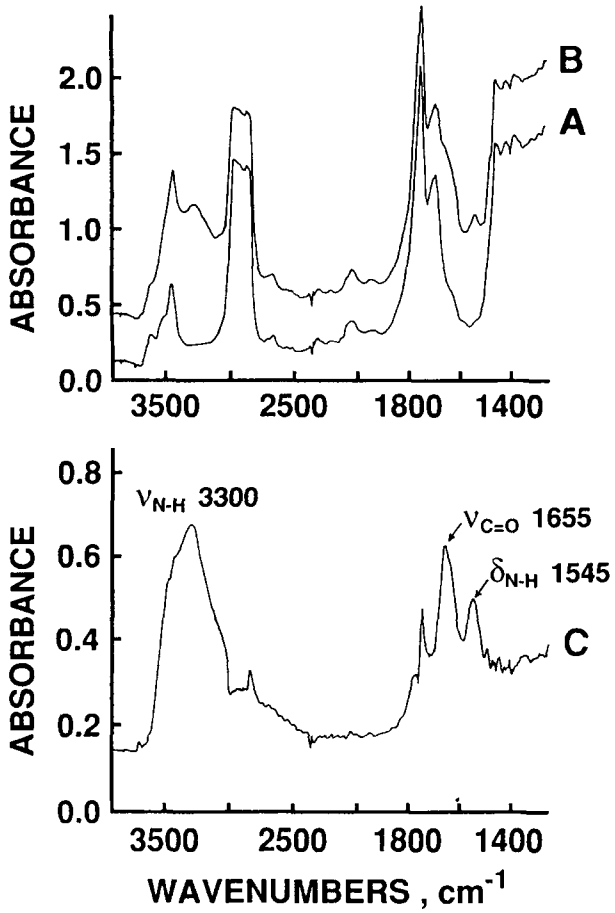


Figure 6 Microscope FTIR surface reflectance spectra of a film of polyester **5c** before and after soil burial test. Film thickness, 140 μm. (A) Original film, M_n, 2.6×10^4, M_w/M_n, 1.5. (B) After 30 days, M_n, 2.5×10^4, M_w/M_n, 1.6. (C) Difference spectrum.

eroded. In contrast, in the cycloheximide-treated soil (C) in which bacteria were supposed to be active, the films of polyesters **5b** and **5c** were degraded, whereas the film of polyester **5d** was scarcely eroded, although the film became slightly opaque here and there. These findings suggest that polyesters **5b** and **5c** are degraded by both filamentous fungi and bacteria, whereas polyester **5d** is primarily degraded by filamentous fungi, consistent with the electron microscopic observation.

Enzymatic Degradation

Enzymatic degradation of polymers is often used for rapidly evaluating the biodegradability of polymers, although it does not exactly reflect degradation under the natural environment. In the present investigation, enzymatic degradation of some of the polyesters was tested by using *R. delemar* lipase, an enzyme which was reported to efficiently degrade aliphatic polyesters such as poly(ε-caprolactone),[16] poly(4-hydroxybutylate),[17] and poly(butylene adipate).[18] Enzymatic degradability was evaluated by the measurement of TOC (total organic carbon) of the water-soluble organic compounds produced by enzymatic degradation of polyesters. The results are presented in Figure 9.

The ordinate of the figure represents the net TOC values corrected by subtracting the TOC values found in the blank tests. Among the eight different polyesters tested, polyester **5d** based on 1,4 : 3,6-dianhydro-D-glucitol and sebasic acid shows the highest TOC value of 890 ppm. The other polyesters were hardly or very slightly degraded by the *R. delemar* lipase. However, it is to be noted here that the polyesters derived from 1,4 : 3,6-dianhydro-D-mannitol were difficult to finely pulvelize and therefore the total surface areas on which the enzyme

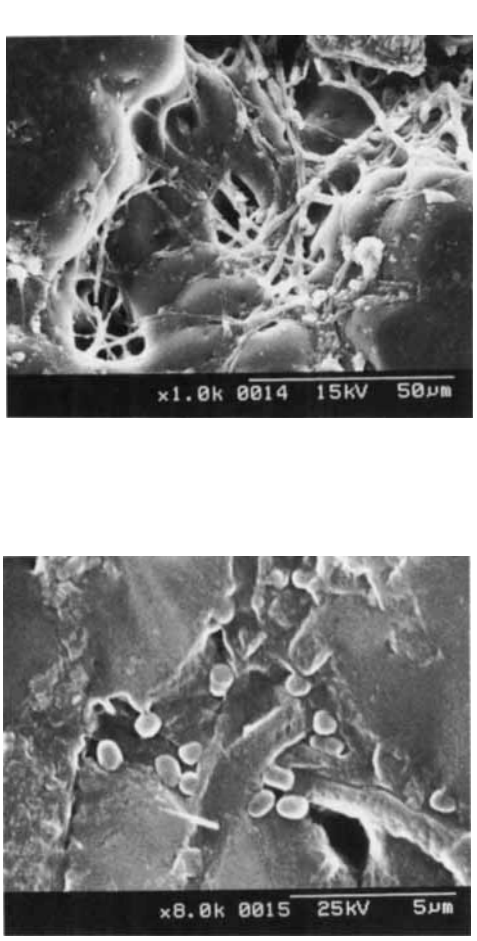


Figure 7 Scanning electron micrograph of polyester **5c** recovered after soil burial for 10 days. Film thickness, 140 μm; M_n, 2.6×10^4; magnification: (A) ×1000; (B) ×8000.

could interact were smaller than those of the polyesters based on **1**.

As described above, *R. delemar* lipase is effective in degrading poly(4-hydroxybutyrate), whereas it is inactive to poly(3-hydroxybutyrate), having a pendant methyl group in each repeating unit. This means that the steric hindrance caused by the pendant methyl groups prevents the active site of the enzyme from approaching the ester bonds in the main chain. The polyesters investigated here contain the bulky and rigid, bicyclic ether units along the polymer chains, and, therefore, the active site of the enzyme may not be able to approach the ester bonds in the polyesters containing the diacid units with shorter methylene chains such as succinic and glutaric acids. However, in view of the findings that these polyesters were degraded in the aforementioned soil burial tests, it seems likely that by proper selection of enzymes these polyesters are also enzymatically degraded.

The foregoing results led us to the conclusion that most of the polyesters synthesized from 1,4 : 3,6-dianhydrohexitols and aliphatic dicarboxylic acids were biodegradable and that their biodegradability varied widely depending on their molecular structures. In particular, polyesters **5d** and **6d** derived from dianhydroglucitiol **1** and sebacoyl dichloride and from dianhydromannitol **2** and sebacoyl dichloride, respectively, were rapidly biodegraded. Although polyesters **7b–7d** based on **3** were not appreciably degraded under the conditions examined, these polyesters are also potentially biodegradable, because 1,4 : 3,6-dianhydro-L-iditol (**3**) itself was found to be catabolized in an activated sludge to carbon dioxide and water. Actually, replacement of some of 1,4 : 3,6-dianhydro-L-iditol units with 1,4 : 3,6-dianhydro-D-glucitol units along the polymer chains by copolycondensation made the polyesters amorphous and biodegradable.[19] The experimental results described herein would give us hope that practically applicable, biodegradable polyesters will be produced from renewable biomass resources in a near future.

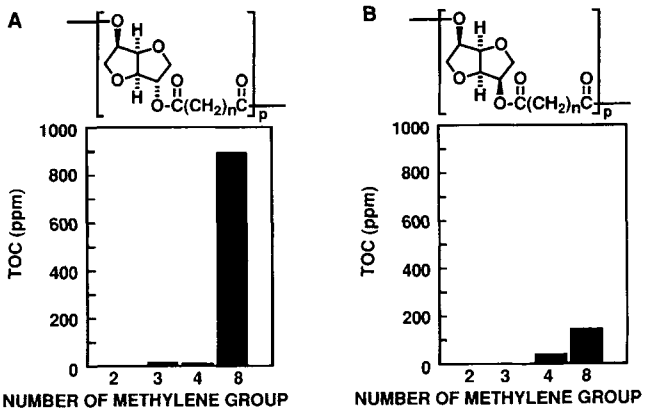


Figure 9 Enzymatic degradation of (A) polyesters **5a–5d** and (B) polyesters **6a–6d** by *R. delemar* lipase. Temp, 37°C; pH 7.0; time 24 h.

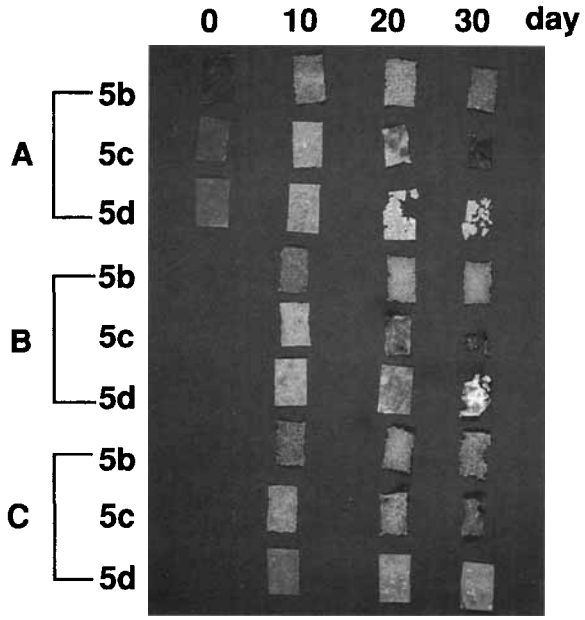


Figure 8 Soil burial degradation of polyesters **5b–5d.** Film thickness 140 μm. (A) Untreated soil; (B) soil treated with streptomycin; (C) soil treated with cycloheximide.

The authors express their sincere gratitude to Professor Makoto Kimura of Nagoya University for his helpful suggestion and discussion on the soil burial degradation tests and Miss Hiroyo Nishide for her technical assistance. Thanks are also due to Professors Yasuo Yuki and Sadao Hibi of Nagoya Institute of Technology for their kind help in the measurements of the thermal and mechanical properties of the polyesters, respectively. The authors thank Dr. Yoshito Ohtake of the Chemical Inspection & Testing Institute for the measurement of microscope FTIR surface reflectance spectra. Financial support from the Ministry of Education, Science and Culture of Japan (Grant-in-Aid for Development Scientific Research, No. 06555286) is gratefully acknowledged.

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Received April 17, 1996
Accepted July 3, 1996