Biodegradable Polymers Based on Renewable Resources. III. Copolyesters Composed of 1,4:3,6-Dianhydro-D-glucitol, 1,1-Bis(5-carboxy-2-furyl)ethane and Aliphatic Dicarboxylic Acid Units

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ABSTRACT: Various copolyesters were synthesized by bulk polycondensation of the respective combinations of 1,4;3,6-dianhydro-D-glucitol (**1**) as the diol component and 1,1-bis[5-(methoxycarbonyl)-2-furyl]ethane (**3b**) and seven dimethyl dialkanoates with methylene chain lengths of 4, 5, 6, 7, 8, 10, and 12 (**4a–4g**) as the dicarboxylic acid components. Most of the copolyesters were amorphous, while a copolyester composed of **1**, **3b**, and dodecanedioic acid (**4g**) (**3b**:**4g** = 25:75) units as well as homopolyesters derived from **1** and azelaic acid (**4d)**, sebacic acid (**4e**), and dodecandioic acid (**4g**), respectively, were partially crystalline. All these homo- and copolyesters were soluble in chloroform, dichloromethane, pyridine, trifluoroacetic acid, and *m*-cresol. The number-average molecular weights of these polyesters were estimated to be in the range of 10,000–20,000 by SEC using chloroform as an eluent and standard polystyrene as a reference. The biodegradability of these copolyesters was assessed by enzymatic degradation using four different enzymes in a phosphate buffer solution at 37°C and by soil burial degradation tests in composted soil at 27°C. In general, biodegradability of the copolyesters decreased with increase in the difuran dicarboxylate **3b** content. Copolyesters containing sebasic acid **4e** units showed higher biodegradability. Soil burial degradation in the soil that was treated with antibiotics, together with electron microscopic observation, indicated that actinomycetes are mainly responsible for the degradation of the copolyesters containing **3b** units in the present soil burial test. J Appl Polym Sci 74: 3342–3350, 1999

Key words: biodegradable polymer; copolyester; furan derivative; glucose derivative; enzymatic degradation

INTRODUCTION

In view of the progressive depletion of fossil resources on Earth, it seems urgently necessary to develop alternative strategies based on the exploitation of renewable resources, biomass, which has not received much attention so far. For instance, furan derivatives can be prepared from renewable plant resources and therefore they are available widely and continuously. Furfural, a versatile member of a furan family, which is obtained from polymeric pentoses by acid-catalyzed hydrolysis followed by acid-catalyzed dehydration, can be chemically trans-

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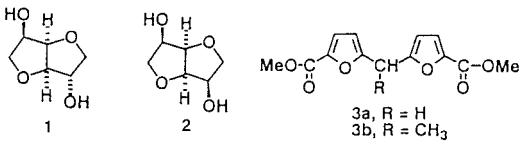
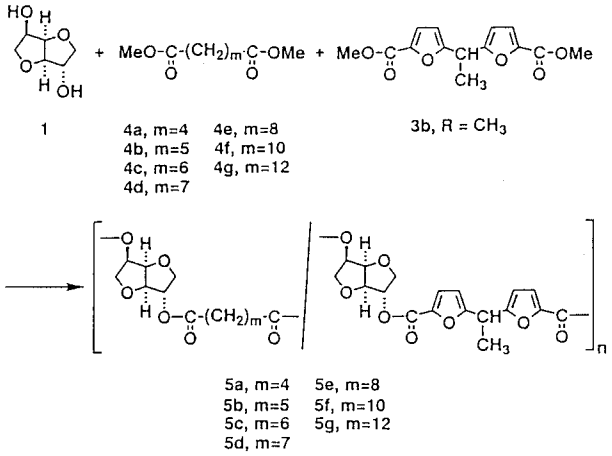
formed in various ways to give monomers for polymer synthesis as well as useful intermediates for organic syntheses.[1–4] Recently, Gandini et al.[5] comprehensively reviewed furan in polymer chemistry. As to the synthesis of polyesters containing furan rings in the main chains, Moore et al.[6–9] reported the synthesis of a series of furan-containing polyesters by polycondensations using furan dicarboxylic acid derivatives and/or dihydroxymethyl furan derivatives. Hirai[10] obtained oligomeric linear and cyclic polyesters by the polycondensation of 5-(hydroxymethyl)-2-furoic acid. Storbeck and Ballauff[11] synthesized polyesters of high glass transition temperature from 2,5-furandiyldicarbonyl dichloride and 1,4;3,6-dianhydrohexitols. Khrouf et al.[12] reported polyester synthesis by transesterification involving difuranic diesters and aliphatic diols.

In the course of a series of investigations on the synthesis of biodegradable polymers based on renewable resources,[13–15] we also synthesized 11 different polyesters by bulk polycondensation of various combinations of 1,4:3,6-dianhydro-D-glucitol (**1**) and 1,4:3,6-dianhydro-D-mannitol (**2**), four aliphatic diols, and three oligo(ethylene glycol)s with bis[5-(methoxycarbonyl)-2-furyl]methane (**3a**) and 1,1-bis[5-(methoxycarbonyl)-2-furyl]ethane (**3b**).[16] These polyesters were amorphous and dissolved in various common organic solvents. Some of them underwent, although very slowly, soil burial degradation. SEM observation of the sample surfaces after the soil burial test, along with enzymatic degradation tests using lipase from *Porcine pancreas*, indicated that all these furan-containing polyesters are, to varying degrees, biodegradable. To improve their biodegradability, we synthesized a variety of copolyesters **5** composed of 1,4;3,6-dianhydro-D-glucitol (**1**) as the diol component and difuranic diester **3b** and seven dimethyl esters of aliphatic dicarboxylic acids **4a–4g** with methylene chain lengths of 4, 5, 6, 7, 8, 10, and 12 as the diester components. The present article describes the syntheses of these copolyesters and their biodegradability as assessed by both enzymatic degradation and soil burial degradation:





EXPERIMENTAL

Materials

Commercially available 1,4:3,6-dianhydro-D-glucitol (**1**) was purified by repeated recrystallization from chloroform. 1,1-Bis[5-(methoxycarbonyl)-2-furyl]ethane (**3b**) was prepared by the reaction of methyl 2-furoate with paraldehyde in concentrated sulfuric acid according to the procedures described in the literature.[17,18] It was purified by recrystallization in methanol. Dimethyl esters of aliphatic dicarboxylic acids were prepared by acid-catalyzed esterification in methanol and purified by distillation.

Polycondensation

Polycondensation was carried out in bulk at 220 or 230°C, first at normal pressure for 6 h, then under reduced pressure (ca. 25 mmHg) by an aspirator for 2 h, and, finally, under a vacuum (1 mmHg) for 16 h. The resulting polymer was isolated by dissolving the reaction mixture in chloroform and pouring the solution into a large volume of methanol. It was purified by repeated reprecipitation using chloroform and methanol as a solvent-and-precipitant pair. It was dried under reduced pressure to a constant weight.

Characterization

Molecular weights of the polyesters were estimated by size-exclusion chromatography (SEC) using chloroform as an eluent and standard polystyrene as a reference. ^{1}H- and ^{13}C-NMR spectra

of the polyesters were taken by JEOL JNM-EX-270 and Bruker ARX-400 instruments operating at 270 and 400 MHz (^{1}H), respectively, on solutions in deuteriochloroform using tetramethylsilane as an internal reference. Surfaces of the polyester films after degradation tests were observed with Hitachi S-4500 and JEOL JSM-F7 scanning electron microscopes. Thermal properties of the polyesters were examined with a Seiko-Electronics DSC-6100 differential scanning calorimeter and a TGA-6200 thermogravimetric analyzer. The total organic carbon contents in aqueous solutions produced by enzymatic degradation of the polyesters were determined with a Shimadzu TOC-500A instrument.

Soil Burial Degradation

Soil burial degradation tests were undertaken on thin films (10 × 25 mm; thickness 140 μm). Polyesters that could not be cast into film were compression-molded into disks (diameter 10 mm; thickness 0.5 mm). The films and disks were buried in soil in a desiccator, in which the relative humidity was adjusted to 70–80% with a saturated aqueous 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 soil 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 by SEC.

Enzymatic Degradation

A 25-mg amount of a powdery sample or a film (thickness 100 μm) was placed in each test tube with a screw cap, to which a phosphate buffer solution of pH 7.0 (10 mL) and the enzyme (250 or 25 units) were added. The test tubes were incubated with constant shaking at 80 strokes/min for 24 h at 37°C. As blank tests, test tubes containing either only the sample or the enzyme were shaken under the same conditions. Hydrochloric acid (1*N*, 3 mL) was added to each mixture, and the total organic carbon content dissolved in the buffer was determined with a TOC instrument. The net TOC values due to enzymatic hydrolysis were determined by subtracting the TOC values in the blank test from the total TOC values.

RESULTS AND DISCUSSION

Syntheses of Copolyesters

As an extension of the study on the synthesis of furan-containing polyesters,[16] we synthesized a series of copolyesters by polycondensation of 1,4:3,6-dianhydro-D-glucitol (**1**) with difuranic diester **3b** and dimethyl dialkanoates **4a–4g** of different methylene lengths. The polycondensations were carried out at 220 or 230°C in the presence of titanium isopropoxide or tetrabutyl-1,3-dichlorodistannoxane as catalysts. Table I summarizes the results of the polycondensations. In each series of the respective dimethyl dialkanoates, we synthesized copolyesters of three different compositions, that is, the mol fractions of the aliphatic ester component in the diester components were about 0.75, 0.50, and 0.25. In most cases, copolyesters were obtained in nearly quantitative yields. In a few cases, however, gelation occurred to some extent, thus resulting in the decrease in the yield of soluble polymer. The number-average molecular weights of these copolyesters were estimated to be up to about 20,000 by SEC using a polystyrene standard.

The homopolyesters derived from **1** and **4d**, **4e**, and **4g**, respectively, were partly crystalline. The other homopolyesters as well as copolyesters were all amorphous, except the copolyester composed of **1**, **3b**, and **4g** (**3b**:**4g** = 25:75). In each series, the glass transition temperature increased with increase in the content of the difuranic component **3b**. The glass transition temperature of the homopolyester consisting of **1** and **3b** is as high as 112°C. All the polyesters and copolyesters containing **1** began to decompose at about 330–340°C, probably due to the decomposition of 1,4:3,6-dianhydro-D-glucitol moieties.

All these homo- and copolyesters are soluble in chloroform, dichloromethane, pyridine, trifluoroacetic acid, and *m*-cresol. Homopolyesters and copolyesters containing dialkanoate units with a shorter methylene chain, **4a–4e,** dissolve in a variety of solvents including 1,4-dioxane, tetrahy-

Table I Bulk Polycondensation of 1,4 : 3,6-Dianhydro-D-glucitol (1) with 1,1-Bis(5-(methoxycarbonyl)-2-furyl)ethane (3b) and Dimethyl dialkanoate (4)

4	Fraction of **4** in Feed[a]	$Ti(OiP)_4$ (mol %)	Temperature (°C)	Yield %	Fraction of **4** in Polymer[b]	M_n [c] ($\times 10^{-3}$)	M_w [c] ($\times 10^{-3}$)	T_g [d] (°C)	T_m [d] (°C)
4a	1.00	0.1	230	98	1.00	14.0	29.6	22	—
4a	0.75	0.1	230	96	0.70	10.0	17.7	41	—
4a	0.52	0.1	230	92	0.46	11.0	21.4	59	—
4a	0.25	0.1	230	87	0.18	9.7	20.0	66	—
4b	1.00	0.1	230	88	1.00	12.1	19.7	12	—
4b	0.75	0.1	230	94	0.73	9.5	20.2	21	—
4b	0.50	0.1	230	98	0.57	9.8	18.2	31	—
4b	0.25	0.1[f]	220	96	0.21	10.2	21.6	42	—
4c	1.00	0.1	230	88	1.00	18.1	28.4	10	—
4c	0.76	0.1	230	94	0.76	16.1	29.7	35	—
4c	0.50	0.1	230	96	0.48	15.1	26.8	43	—
4c	0.25	0.1	230	98	0.24	11.3	27.6	56	—
4d	1.00	0.1	230	99	1.00	16.1	24.9	1	54
4d	0.75	0.1	230	99	0.76	15.8	25.2	15	—
4d	0.50	0.1	230	97	0.48	10.0	18.8	26	—
4d	0.25	0.1	230	95	0.20	10.5	22.1	36	—
4e	1.00	0.1	230	86	1.00	13.3	26.4	−10	50
4e	0.75	0.1	230	83	0.79	11.7	23.3	13	—
4e	0.50	0.1	230	90	0.52	17.1	33.4	24	—
4e	0.25	0.1	230	89	0.27	9.9	22.2	53	—
4f	1.00	0.1	230	92	1.00	15.9	23.1	−9	—
4f	0.75	0.1	230	76	0.63	20.5	30.7	12	—
4f	0.50	0.1	230	89	0.54	14.5	26.1	22	—
4f	0.25	0.1	230	90	0.20	10.0	18.6	49	—
4g	1.00	0.1	220	86	1.00	20.6	31.5	−13	70
4g	0.75	0.1	220	94	0.75	18.7	36.0	2	50
4g	0.50	0.1	220	68	0.51	12.7	23.3	24	—
4g	0.25	0.1	220	50	0.22	12.4	24.4	27	—
—	0.00	0.25	230	85	0.00	7.8	20.5	112	—

1,4 : 3,6-Dianhydro-D-glucitol (**1**), 1.7–7.0 mmol; total diesters, 1.7–7.0 mmol; reaction time, 6 h/760 mmHg, 2 h/25 mmHg, and 16 h/1 mmHg.

[a] Mole fraction of dialkanoate **4** in the dicarboxylic acid components in feed.

[b] Mole fraction of dialkanoate **4** in the dicarboxylic acid units in copolymer. Determined by ^{1}H-NMR ($CDCl_3$, 10%, TMS 270 MHz).

[c] Determined by SEC in $CHCl_3$ (polystyrene standard).

[d] Determined by DSC (heating rate, 10°C/min).

[e] Tetra-*n*-butyl-1,3-dichlorodistanoxane.

drofuran, acetonitrile, dimethylformamide, dimethyl sulfoxide, and sulfolane, in addition to the solvents mentioned above. Homopolyesters containing dialkanoate units with a longer methylene chain, **4f** and **4g,** are insoluble in dipolar aprotic solvents, but soluble in benzene and toluene. In most cases, the solubility became increasingly lower with the increase in the difuranic diester **3b** content. The exception is the solubility of polyesters of the **4f** and **4g** series, where the homopolyesters composed of **1** and **4f** or **4g** are the least soluble. They are insoluble in dimethyl sulfoxide, dimethylformamide, and sulfolane. The partial crystallinity and increased hydrohobicity of these polyesters are responsible for the reduced solubility in these dipolar aprotic solvents.

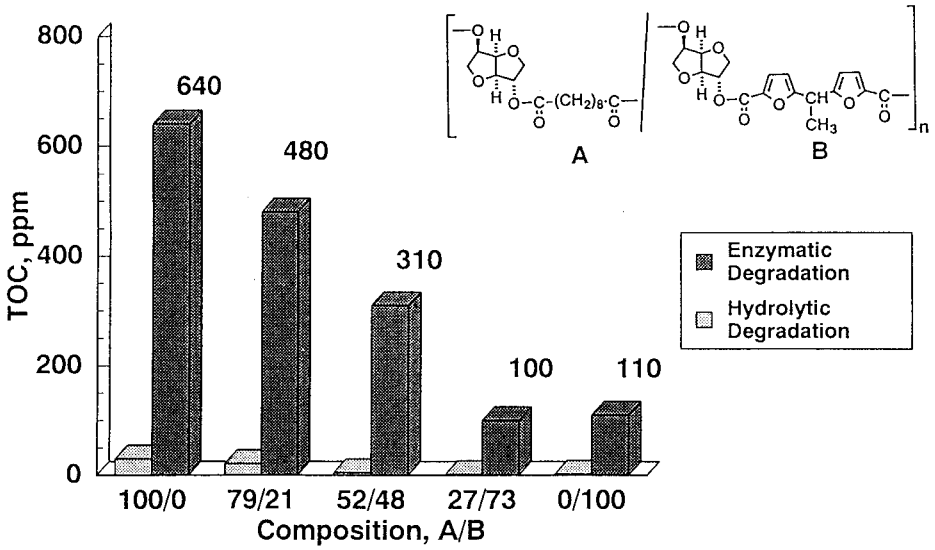


Figure 1 Enzymatic degradation of polyesters **5e** by *P. pancreas* lipase. Conditions: lipase, 250 units; polyester, 25 mg; film thickness, 100 μm (polyester of A/B = 0/100, powder); phosphate buffer (pH 7.0), 2 mL; incubated at 80 strokes/min at 37°C for 24 h.

Biodegradability of Copolyesters

Enzymatic Degradation

Enzymatic degradability was evaluated by the measurement of total organic carbon content (TOC) of aqueous solutions containing water-soluble degradation products. Figure 1 presents the results of the enzymatic degradation of the homo- and copolyester films composed of dianhydroglucitol **1**, difuranic diester **3b**, and sebacate **4e** units using *P. pancreas* lipase in a phosphate buffer solution. As the graph shows, hydrolytic degradation of these polyesters was negligibly small under the conditions examined. The bars showing the TOC value due to the enzymatic degradation were corrected for the hydrolytic degradation by subtracting the corresponding TOC value due to hydrolytic degradation from the observed TOC value. These data clearly demonstrate that the homopolyester composed of **1** and **4e** is most easily degraded and that the degradation becomes increasingly slower as the content of the difuranic diester component **3b** increases.

Figure 2 shows the results of the enzymatic degradation of polyester films of the same series of polyesters using *Rhizopus delmar* lipase in a phosphate buffer solution. In this case, the homopolyester composed of dianhydroglucitol **1** and sebacate **4e** underwent enzymatic degradation at a much higher rate than did the copolyesters. In other words, *R. delemar* lipase shows a higher substrate selectivity than that of *P. pancreas* lipase, shown in Figure 2. This enzyme originates from filamentous fungi, and, therefore, the dramatic reduction of enzymatic degradability by the incorporation of a relatively small fraction of the difuranic units **3b** in the polymer suggests that these copolyesters are reluctant to degrade by filamentous fungi. This point will be described in a later section dealing with soil burial degradation.

Figure 3 presents the results on the enzymatic degradation of the homopolyester from 1,4:3,6-dianhydro-D-glucitol (**1**) and dimethyl sebacate (**4e**) and the corresponding copolyester containing a small fraction of the difuranic diester unit **3b** by two enzymes, *Pseudomonas sp*. lipase and *Pseudomonas sp*. cholesterol esterase. Judging from the TOC values shown in Figure 4, the homopolyester is much more easily degraded by these enzymes. However, introduction of 21 mol % of the difuranic ester component **3b** dramatically decreased the enzymatic degradability of the polyester, indicating that these enzymes show higher substrate selectivity than that of *R. delemar* lipase and *P. pancreas* lipase.

Figure 4 compares the results on the enzymatic degradation of all the copolyesters using *P. pancreas* lipase. Although it is difficult to generalize the structure–enzymatic degradability of these

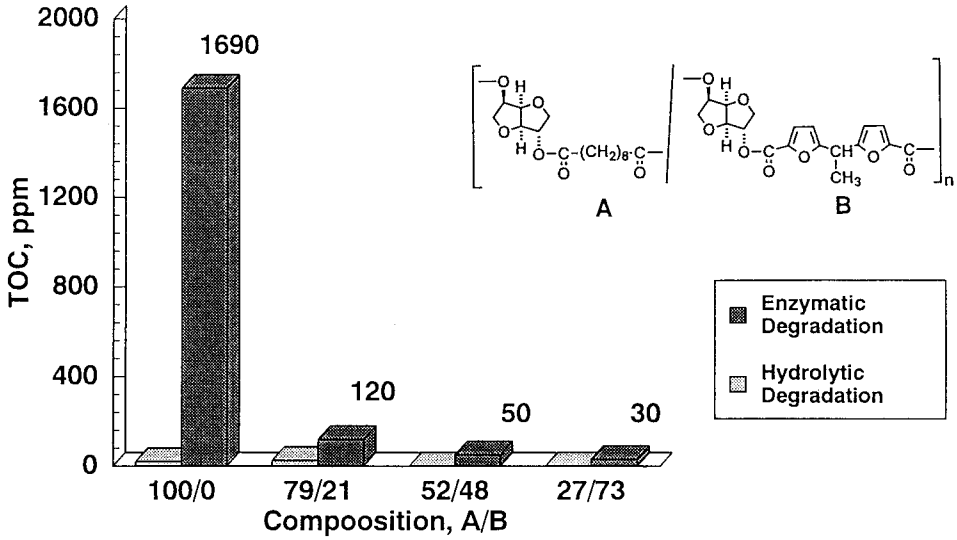


Figure 2 Enzymatic degradation of polyesters **5e** by *R. delemar* lipase. Conditions: lipase, 250 units; polyester, 25 mg; film thickness, 100 μm; phosphate buffer (pH 7.0), 2 mL; incubated at 80 strokes/min at 37°C for 24 h.

copolyesters, the higher the dialkanoate content in the dicarboxylic acid components, the easier is the enzymatic degradation. The observed fluctuation of the biodegradability with increase in the methylene chain length of the aliphatic diacid component in the copolyesters appears complex and cannot be interpreted in a simple manner. It is noteworthy that the TOC values became maximum for the polyesters with a methylene chain length of 8 in the dialkanoate units, except for the copolyesters of the aliphatic unit/difuranic unit ratio of 25/75 in the diacid components. Presumably, the decrease in the steric requirement and the increase in the mobility of polymer chains with increasing methylene chain length favors the accessibility of the enzyme to the ester linkages to be cleaved, while the optimum hydrophilic–hydrophobic balance is needed for efficient

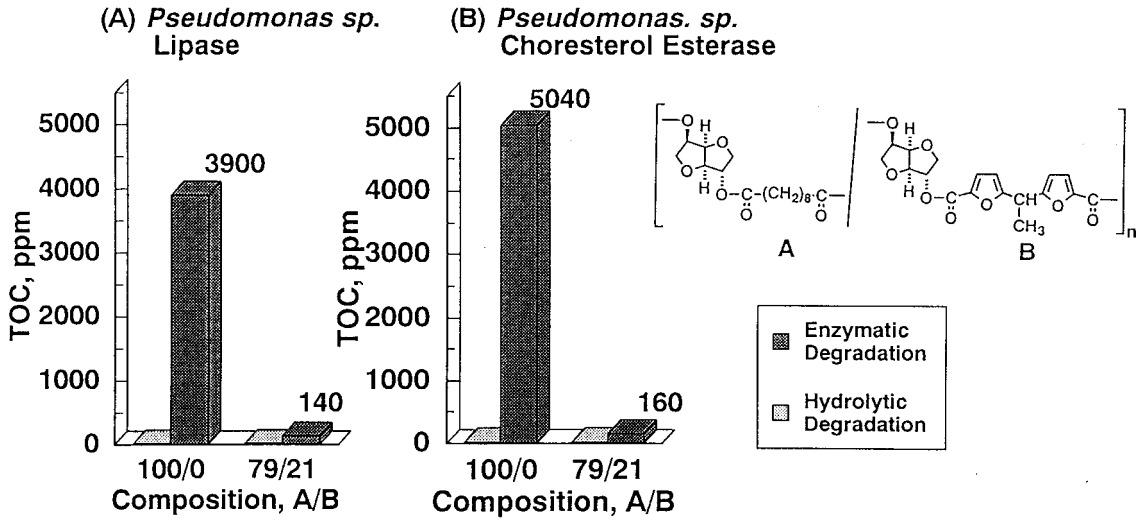


Figure 3 Enzymatic degradation of polyesters **5e** by enzymes from *Pseudomonas sp.*: (A) *Pseudomonas sp.* lipase; (B) *Pseudomonas sp.* cholesterol esterase. Conditions: enzyme, 25 units; polyester, 25 mg (film thickness 100 μm); phosphate buffer (pH 7.0), 2 mL; incubated at 80 strokes/min at 37°C for 24 h.

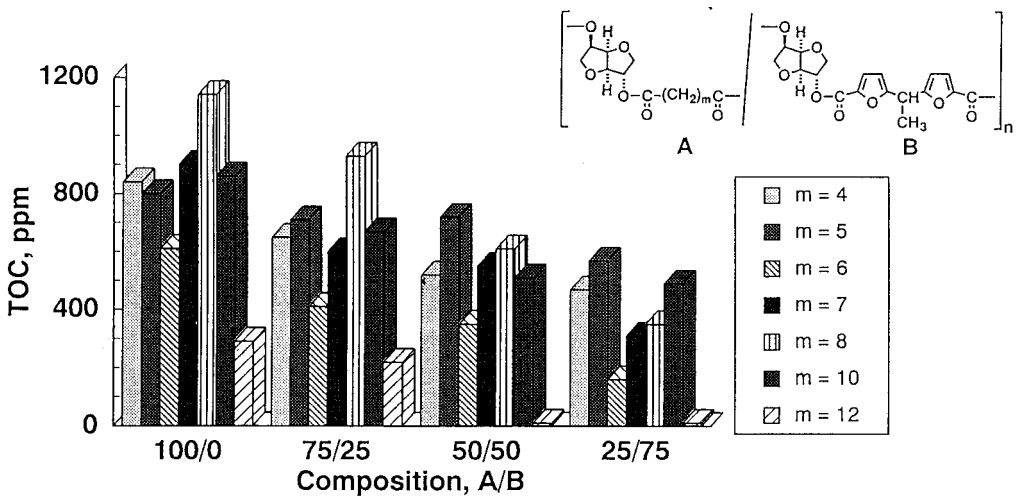


Figure 4 Enzymatic degradation of polyesters **5a–5g** by *P. pancreas* lipase. Conditions: lipase, 250 units; polyester, 25 mg; film thickness, 100 μm; phosphate buffer (pH 7.0), 2 mL; incubated at 80 strokes/min at 37°C for 24 h.

binding. Homo- and copolyesters containing the longest dodecamethylene chain showed appreciably lower enzymatic degradability than that of the other copolyesters. In these polyesters, the higher hydrophobicity seems to make the approach of the enzyme to the substrate unfavorable.

Soil Burial Degradation

The soil burial test was carried out at 27°C in the soil which had been composted for more than 10 years at the Nagoya University farm. Figure 5 shows the results on the soil burial degradation of the series of polyesters based on **1**, **3b**, and **4e** units. The film of the homopolyester consisting of **1** and **4e** units was almost completely degraded after the soil burial for 1 month. The copolyesters became less degradable with increase in the **3b** content. Actually, the homopolyester consisting of **1** and **3b** units was negligibly degraded even after prolonged soil burial. The soil burial test of this homopolymer was

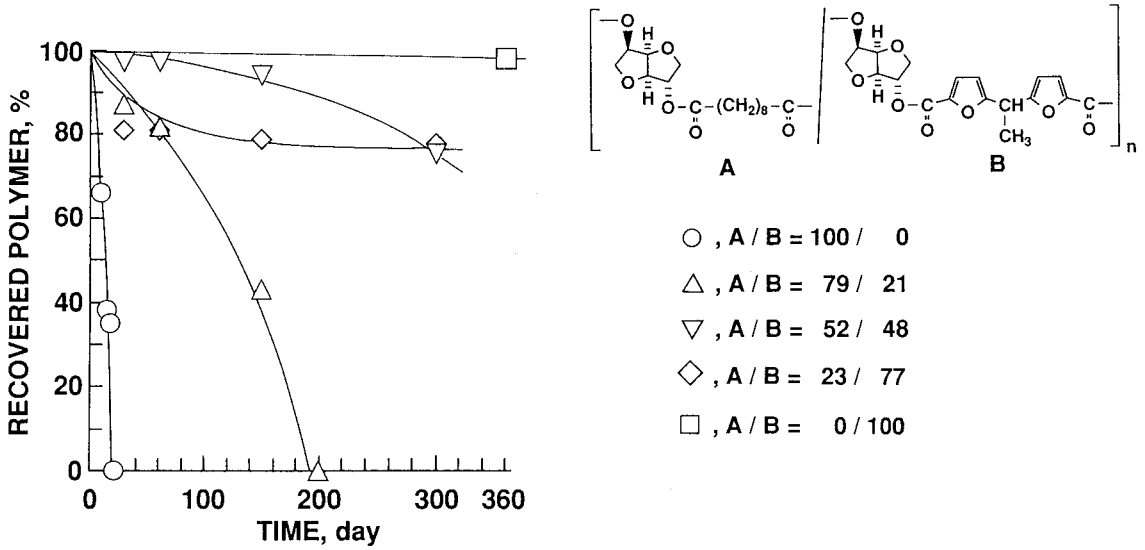


Figure 5 Recovery (wt %) of polyesters **5e** in soil burial degradation test. Conditions: film thickness, 100 μm (disk thickness 0.5 mm for polyester of A/B = 0/100); composted soil, pH 7.4; temperature, 27°C; humidity, 70–80%.

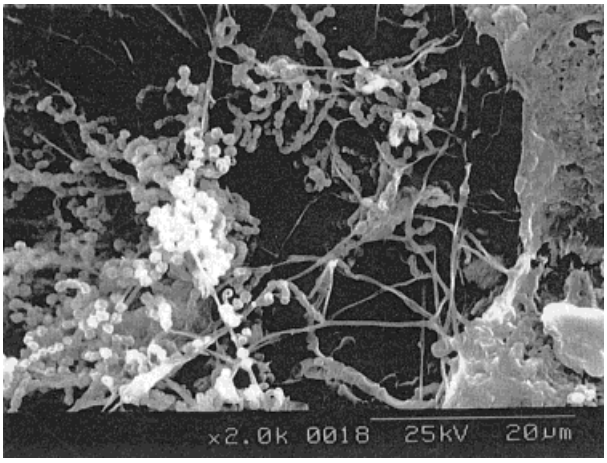


Figure 6 SEM photograph of copolyester **5e** (**3b** : **4e** = 21 : 79) recovered after soil burial for 30 days. Conditions: film thickness, 100 μm; composted soil, pH 7.4; temperature, 27°C; humidity, 70–80%.

carried out on disks, because thin films could not be prepared by casting. Therefore, strict comparison cannot be made between this homopolyether and other homo- and copolyesters.

Figure 6 shows an SEM photograph of the copolyester film of the composition of **3b**:**4e** = 21:79 after soil burial for 30 days. A colony of actinomycetes with spores and hyphae can be seen clearly. As described above, the homopolyester exclusively consisting of **1** and **3b** units was hardly degraded in the soil burial test under similar conditions. Nevertheless, numerous spores and hyphae of actinomycetes were observed on the surface of the homopolyester disk, indicating that the homopolyester should be degraded, although very slowly, by actinomycetes.

To determine whether either bacteria or filamentous fungi or both are responsible for the soil burial degradation of these furan-containing polyesters, we examined the effect of added antibiotics on the soil burial degradation of copolyesters **5e** using three series of samples. The samples in Series A are the films buried in the composted soil without antibiotic, the samples in Series B are the films buried in streptomycin (an antibacterium)-treated soil (1 mg/g), and the samples in Series C are the films buried in cycloheximide (an antifungus)-treated soil (1 mg/g). The results are summarized in Table II.

In the streptomycin-treated soil (Series B), in which filamentous fungi are supposed to be active, degradation was retarded considerably. On the contrary, in the cycloheximide-treated soil (Series C), in which actinomycetes and bacteria are supposed to be active, degradation proceeded to a level similar to, or even greater than, the degradation in the soil without added antibiotic (Series A). SEM inspection of the polyester films after soil burial for 30 days revealed that there were spores and hyphae of actinomycetes on the surfaces of the films that had been buried in the soil without antibiotics (Series A), whereas they were not detectable on the surface of the film that had been buried in the streptomycin-treated soil (Series B). In contrast, colonies of actinomycetes were observed along with a small number of bacteria on the surfaces of the polyester films that had been buried in the cycloheximide-treated soil (Series C). In all three series, no filamentous fungi were observed by SEM. This is consistent with the expectation from the enzymatic degradation experiment described above. Therefore, we can conclude that actinomycetes are mainly responsible for the degradation of the polyester and copolyesters containing difuranic units **3b** in the present soil burial degradation test.

Table II Effect of Antibiotics on the Soil Burial Degradation of Copolyester 5e (3b : 4e = 21 : 79)

		After 30 Days		SEM Observation		
Antibiotic	Initial M_n^0 ($\times 10^3$)	Recovery, (%)	M_n/M_n^0 (%)	Actinomycetes	Bacteria	Filamentous Fungi
None	17.0	87	99	Present	Present[a]	Absent
Streptomycin	17.0	97	100	Absent	Absent	Absent
Cycloheximide	17.0	77	96	Present	Present[a]	Absent

Composted soil, pH 7.4; temperature, 27°C; film thickness, 100 μm.
[a] A small number of bacteria were observed on the surface of the recovered film.

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