Biodegradable Polymers Based on Renewable Resources. VI. Synthesis and Biodegradability of Poly(ester carbonate)s Containing 1,4:3,6-Dianhydro-D-glucitol and Sebacic Acid Units

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ABSTRACT: Poly(ester carbonate)s with different compositions were synthesized by bulk polycondensation of 1,4:3,6-dianhydro-D-glucitol with diphenyl sebacate and diphenyl carbonate in the presence of zinc acetate as a catalyst. Most of the poly(ester carbonate)s as well as the corresponding polycarbonate were amorphous, except the poly(ester carbonate) with a small carbonate content and the corresponding polyester, which are semicrystalline. All these poly(ester carbonate)s are soluble in chloroform, pyridine, dimethylformamide, dimethyl sulfoxide, and *N,N*-dimethylacetamide. Soil burial degradation tests, biochemical oxygen demand (BOD) measurements in an activated sludge, and enzymatic degradation tests indicated that these poly(ester carbonate)s are potentially biodegradable. The biodegradability was found to be maximum for the poly(ester carbonate)s with carbonate contents of 10–20 mol % and to decrease markedly for the poly(ester carbonate)s with the carbonate content above 50 mol %. The biodegradability of the poly(ester carbonate)s is discussed in terms of the crystallinity, glass transition temperature, and surface hydrophobicity of the polymer films. J Appl Polym Sci 86: 872–880, 2002

Key words: biodegradable; polycondensation; polycarbonates; renewable resources; polyesters

INTRODUCTION

Recently, requests for biodegradable polymers have become increasingly greater each day as one of the effective means of reducing global environmental pollution caused by wasted and undegraded plastics. As to synthetic biodegradable polymers, aliphatic polyesters such as poly(butylene succinate), poly(ε-caprolactone), and poly(L-lactide) are commercially produced, and their production continues to increase. Besides these aliphatic polyesters, various types of synthetic biodegradable polymers have been designed and tested. They are, for example, polyesters containing aromatic rings or cyclic ether moieties, poly(ester amide)s, poly(ester carbonate)s, and poly(ester urethane)s.[1]

From the standpoints of the preservation of finite fossil resources and the sustainment of the global environment as well, great concern has been directed toward syntheses of biodegradable polymers based on renewable resources.[2–4] Among a variety of candidate compounds of the plant-based biomass origin, 1,4:3,6-dianhydro-D-glucitol (**1a**), 1,4:3,6-dianhydro-D-mannitol (**1b**), and 1,4:3,6-dianhydro-L-iditol (**1c**) seem to be promising difunctional monomers for polycondensations and polyadditions (Scheme 1). In fact, the former two monomers **1a** and **1b** are readily available from D-glucose and D-mannose, respectively, and have been used for polymer syntheses.[5–10] The last monomer **1c** is derived from **1b** via a Mitsunobu reaction.[11] Using these isomeric diols, we synthesized a series of polyesters **2** and examined their biodegradability in detail.[12–16] Recently, Kricheldorf et al.[17] and we[18] independently synthesized structurally regular poly(ester amide)s **3** from **1a**, α-amino acids, and aliphatic dicarboxylic acids and evaluated their biodegradability. As an extension of the series of our studies on biodegradable polymer syntheses based on renewable plant resources, the present article is concerned with the synthesis and biodegradability of poly(ester carbonate)s **4** based on **1a** and sebacic acid units. Sebacic acid was selected for the acid component in this work, because polyester **2** consisting of **1a** and sebacic acid units had been found to show an excellent biodegradability.[13,16]

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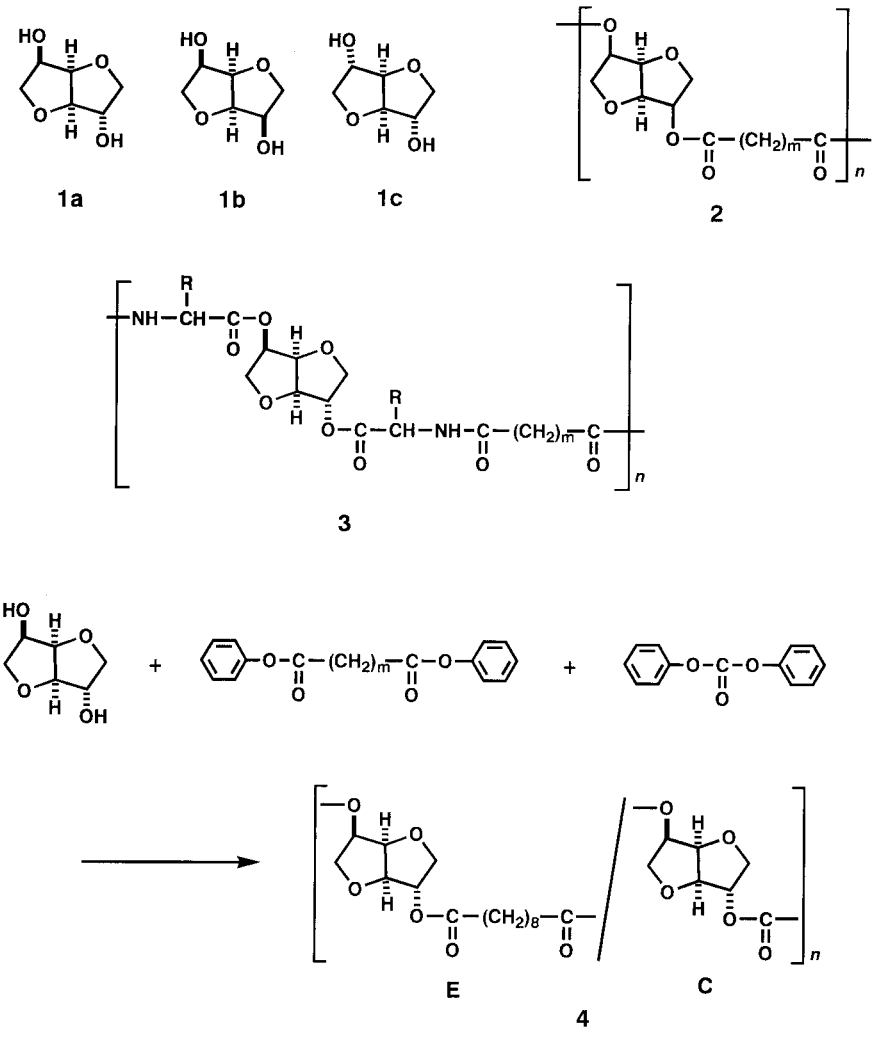


	E/C		E/C
4a	100/0	4d	76/24
4b	93/7	4e	51/49
4c	82/18	4f	0/100

Scheme 1

As for the biodegradation of polycarbonates, Nakano et al. reported that poly(ethylene carbonate) underwent rapid enzyme-mediated bioabsorption *in vivo*, whereas poly(1,2-propylene carbonate) completely suppressed an enzymatic attack.[19,20] Pitt et al. demonstrated that poly(trimethylene carbonate) was degraded by enzymatic action and that the enzymatic cleavage of poly(trimethylene carbonate) was slower than that of poly(ethylene carbonate) but much faster than that of poly(1,2-propylene carbonate).[21] Albertsson and Eklund described that the degradation of poly(trimethylene carbonate) was very slow.[22] Thus, in contrast to the results by Pitt et al., poly(trimethylene carbonate) was not affected by the biological environment (rat) during an implantation time of 180 days. Kricheldorf et al. demonstrated that poly(trimethylene carbonate) showed high biodegradability as evidenced by the decomposition in the peritoneal cavities of rats.[23]

To improve the degradability of poly(alkylene carbonate)s, a variety of poly(ester carbonate)s,[23–30] poly(alkylene carbonate anhydride),[31] and poly(trimethylene carbonate)-*b*-PEG-*b*-poly(trimethylene carbonate)[32] were synthesized, and their degradability was investigated. As to the synthesis of polycarbonates based on **1a**, Kricheldorf et al. prepared a series of cholesteric copolycarbonates by polycondensations of the bischloroformate derivative of **1a** with methylhydroquinone and 4,4′-dihydroxybiphenyl and evaluated **1a** as a chiral building block.[33,34]

EXPERIMENTAL

Materials

Commercially available 1,4:3,6-dianhydro-D-glucitol (**1a**) was purified by repeated recrystallization from chloroform. Diphenyl sebacate was prepared by the reaction of phenol and sebacoyl chloride in acetonitrile in the presence of pyridine and purified by recrystallization from ethyl acetate; mp 69–70°C. Commercially available diphenyl carbonate was purified by recrystallization from ethyl acetate.

Polycondensation

Polycondensations of **1a** with mixtures of diphenyl sebacate and diphenyl carbonate of various molar ratios were carried out in the presence of zinc acetate as a catalyst in a test tube equipped with a three-way stopcock. The reaction mixture was first heated at 190°C for 6 h under normal pressure, then at 20 mmHg for 2 h, and, finally, under a vacuum at 1 mmHg for 16 h. After a designated time, the mixture was dissolved in chloroform, and the solution was poured into methanol to precipitate the polymer. The polymer was purified by the reprecipitation using chloroform and methanol as a solvent and precipitant pair several times and dried under a vacuum.

Characterization

Molecular weights of poly(ester carbonate)s **4** were estimated by size-exclusion chromatography (SEC) using chloroform as an eluent and polystyrene as a reference. ^{1}H-and ^{13}C-NMR spectra of the poly(ester carbonate)s were taken by a VARIAN 3-2 GEMINI 2000 operating at 300 MHz on solutions in deuteriochloroform using tetramethylsilane as an internal reference. Surfaces of poly(ester carbonate) films after soil burial tests were observed with a Hitachi S-2150 scanning electron microscope. Thermal transition temperatures of the poly(ester carbonate)s were determined with a Seiko Instruments DSC 6200 differential scanning calorimeter at a heating rate of 10°C/min. Total organic carbon concentrations (TOCs) in aqueous solutions produced by enzymatic degradation of the polyesters were determined with a Shimadzu TOC-500A instrument. X-ray diffraction diagrams were taken on films by a Shimadzu electron microanalyzer EPMA-1400. Contact angles of water and diiodomethane on the surfaces of poly(ester carbonate) films were measured with a Kyowa Interface Science FASE-CADT contact-angle instrument.

Soil burial degradation

Soil burial degradation tests were undertaken on thin films (10 × 10 mm, thickness 150 μm). The films were buried in soil at a 1-cm depth from the surface 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 depending on the progress of degradation, the films or disks were taken out, washed with water, and dried. When soil adhered to the sample surface 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 recovered polymer was characterized by weight, SEC, and ^{1}H-NMR measurements.

Enzymatic degradation

The enzymes used in the present investigation were *Porcine pancreas* lipase (Sigma Chemical, Tokyo, Japan), *Porcine liver* esterase (Sigma Chemical), *Pseudomonas* sp. lipase (Wako Chemical, Osaka, Japan), *Pseudomonas* sp. cholesterol esterase (Wako Chemical), *Pseudomonas* sp. lipoprotein lipase (Wako Chemical), *Candida rugosa* lipase (Sigma Chemical), *Streptmyces rochei* carboxyesterase (Wako Chemical), Proteinase K (Wako Chemical), and papain (Wako Chemical). They were used as supplied. A powdery sample (25 mg) was taken in each test tube with a screw cap, and a small amount of chloroform 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 polymer. A phosphate buffer solution of pH 7.0 (10 mL) and the enzyme (250 or 25 units) were added to the test tube. The test tube was incubated with constant shaking at 80 strokes per minute 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. The reaction mixture was filtered through a Millipore filter. An aliquot of 100 μL of the filtrate was taken out and diluted with water to 10 mL. The TOCs in the aqueous solutions, produced by enzymatic degradation of the poly(ester carbonate)s, were determined with a Shimadzu TOC-500A instrument.

Biochemical oxygen demand (BOD) test in an activated sludge

An activated sludge was prepared so that the suspension concentration was 30 mg/L according to Japan industrial standard JIS K 6950 (corresponding to ISO 14851), using an activated sludge taken from a sewage plant in Meito-ku, Nagoya. A film sample (thickness, 150 μm; 15 mg) and the activated sludge (150 mL)

TABLE I
Polycondensation of 1,4:3,6-Dianhydro-D-glucitol (1) with Diphenyl Sebacate (E) and Diphenyl Carbonate (C)

No.	**1** (mmol)	$[E]_0/[C]_0$ in feed	Temperature (°C)	Time (h)	Yield (%)	[E]/[C][a] in polymer	M_n[b] $\times 10^{-3}$	T_g[c] (°C)	T_m[c] (°C)	T_d[c] (°C)
4a	2.11	100/0	190	24[d]	95	100/0	20.4	3	48	386
4b	7.54	90/10	190	24[d]	92	93/7	16.2	4	47	352
4c	6.92	80/20	190	24[d]	91	82/18	14.7	18	—	350
4d	7.34	70/30	190	24[d]	94	74/26	10.1	23	—	339
4e	8.27	50/50	190	24[d]	96	51/49	11.4	43	—	329
4f	10/3	0/100	210	11[e]	95	0/100	26.7	166	—	283

[a] Determined by ^{1}H-NMR ($CDCl_3$; 300 MHz).
[b] Determined by SEC ($CHCl_3$; polystyrene standard).
[c] 5% weight loss temperature determined by DSC (heating rate, 5°C/min).
[d] 6 h/760 mmHg, 2 h/20 mmHg, 16 h/1 mmHg.
[e] 2 h/760 mmHg, 1 h/20 mmHg, 8 h/1 mmHg.

were taken in a bottle and the oxygen consumption was measured at 25°C for 28 days by a TITEC, BOD Tester 200F. The BOD-based biodegradability was estimated by the percent of the consumed amount of oxygen corrected for a blank test to the theoretical amount of oxygen required for the complete oxidation of the sample. A model compound for the 1,4:3,6-dianhydro-D-glucitol-carbonate moiety, 1,4:3,6-dianhydro-2,5-bis-*O*-(methoxycarbonyl)-D-glucitol, was treated in the activated sludge in a similar manner and its BOD biodegradability was evaluated.

RESULTS AND DISCUSSION

Synthesis of poly(ester carbonate)s

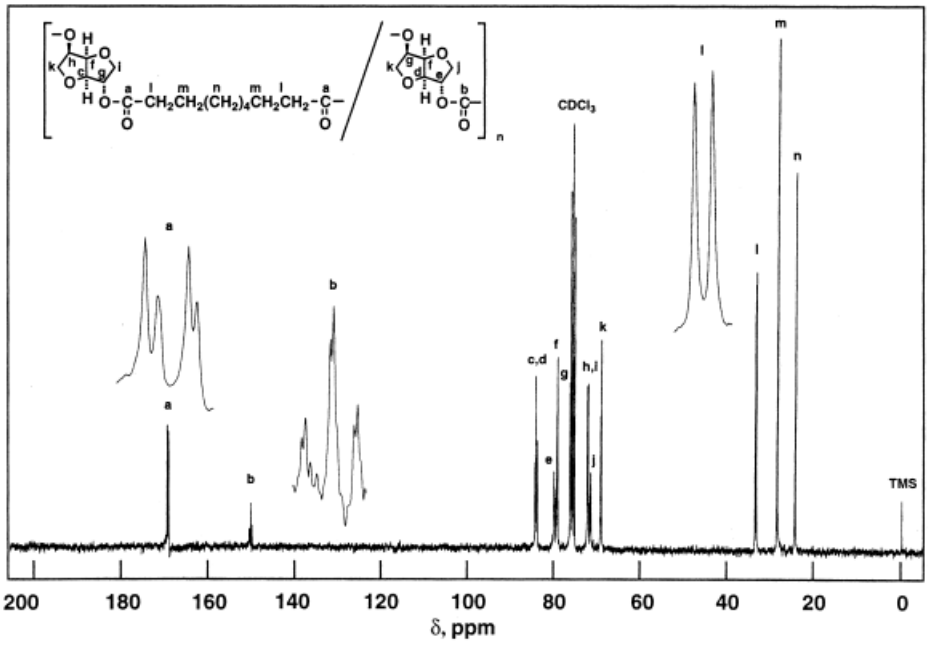
Poly(ester carbonate)s **4** of different compositions were synthesized by polycondensation of **1a** with diphenyl carbonate and diphenyl sebacate using zinc acetate as a catalyst. Some of the data are listed in Table I, together with those of the corresponding polyester and polycarbonate. The polycondensation proceeded relatively smoothly to yield the desired polymers in high yields. Use of titanium tetraisopropoxide or tetrabutyl-1,3-dichlorodistannoxane as catalysts gave lower molecular weight polymers in lower yields.

The number-average molecular weights of the polymers determined by SEC were in the range of 1.0×10^4–2.6×10^4. Polyester **4a** and poly(ester carbonate) **4b** with a 7 mol % carbonate component were partially crystalline, whereas poly(ester carbonate)s **4c–4e** with the higher contents of the carbonate component as well as polycarbonate **4f** were amorphous. The glass transition temperature of poly(ester carbonate)s **4** increased from 3°C for polyester **4a** to 166°C for polycarbonate **4f** as the carbonate content increased. The thermal stability of the polymers, as judged by the degradation onset temperature (5% weight loss), decreased with increase in the carbonate content. Polycarbonate **4f** is soluble in chloroform, pyridine, *N,N*-dimethylformamide, dimethyl sulfoxide, and *N,N*-dimethylacetamide. Poly(ester carbonate)s **4b–4e** and polyester **4a** are soluble also in toluene, tetrahydrofuran, and acetonitrile, in addition to the solvents that dissolve polycarbonate **4f**.

1,4:3,6-Dianhydro-D-glucitol (**1a**) has an *exo*-hydroxyl group in the C(2)-position and an *endo*-hydroxyl group in the C(5)-position, and it is an unsymmetrical molecule. Therefore, the carbonate carbonyl carbon between two units of **1a** lies in the three different configurational situations, that is, between C(2)—C(2), C(2)—C(5), and C(5)—C(5). Figure 1 shows the ^{13}C-NMR spectrum of poly(ester carbonate) **4e** with a carbonate content of 49 mol %. Three signals due to the carbonate carbon atom appeared at δ 154.01, 153.64, and 153.30 ppm with the relative intensities of 1:2:1. This is a clear indication that the units of **1a** are randomly incorporated into the polymer chain with regard to the two reaction sites (i.e., head to head, head to tail, and tail to tail). The ester carbonyl carbon atom signals appeared at 173.6–173.9 ppm as four peaks, as clearly shown in the expanded spectrum. Presumably, the ester carbonyl carbon signal appears at different chemical shifts depending on whether it is connected with an *exo*- or *endo*-exocyclic oxygen of the 1,4:3,6-dianhydro-D-glucitol ring, and each of the signals splits further into two signals with slightly different chemical shifts depending on whether the other exocyclic oxygen of the same 1,4:3,6-dianhydro-D-glucitol ring forms an ester linkage or a carbonate linkage.

Soil burial degradation

The soil burial degradation test was carried out on the films of poly(ester carbonate)s **4** at 27°C in the soil, which had been composted for more than 10 years at Nagoya University farm. Figure 2 depicts the change in the residual polymer weight during soil burial. Clearly, the samples were classified into two groups with regard to the degradability. Thus, poly(ester car-



Peak	δ, ppm
a	173.9, 173.9, 173.7, 173.6
b	154.7, 154.4, 154.1
c	86.9
d	86.3
e	82.2
f	81.5
g	78.5
h	74.4
i	74.3
j	73.6
k	71.3 ~ 70.1
l	34.7, 34.5
m	29.6
n	25.4

Figure 1 ^{13}C-NMR spectrum of poly(ester carbonate) **4e** with the carbonate content of 49 mol %. Solvent, $CDCl_3$; room temperature; 75 MHz.

bonate)s **4a–4d** with carbonate contents up to 26 mol % degraded relatively rapidly in the soil burial. Particularly, poly(ester carbonate)s **4b** with the carbonate content of 7 mol % degraded faster than did polyester **4a**. In sharp contrast, poly(ester carbonate) **4e** with a carbonate content of 49 mol % as well as polycarbonate **4f** degraded very slowly.

Table II lists the changes in the molecular weight and composition of poly(ester carbonate)s **4** before and after the soil burial for 10 days. The molecular weights of the recovered polymers were somewhat higher than were those of the original polymers for four of the six samples. Presumably, this is due to the preferential degradation of the lower molecular weight polymer in the early stage. The change in the molecular weight distribution was not uniform. It increased, if any, slightly for the recovered polymers with 16–25% weight loss, whereas it decreased very slightly for the polymers with lower weight loss. The compositions of the samples hardly changed during the soil burial, although forcibly speaking, the ester content decreased to a small extent.

In general, nonenzymatic hydrolysis causes random cleavage of polymer chains, resulting in the decrease in molecular weight. In contrast, enzymatic hydrolysis proceeds through the surface erosion mechanism involving the adsorption of enzyme on the polymer surface followed by chain cleavage. The data in Table II suggest that poly(ester carbonate)s **4** are degraded chiefly through the surface erosion mechanism by the

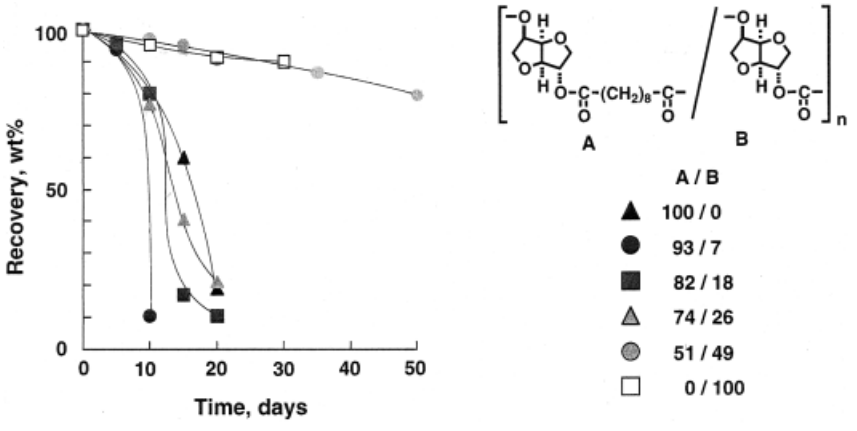


Figure 2 Recovery (weight percent) of poly(ester carbonate)s **4** in soil burial test. Film thickness, 150 μm; composted soil, pH 6.6; temperature, 27°C; humidity, 70–80%.

TABLE II
Changes in the Molecular Weight and Composition of Poly(ester carbonate)s 4 Before and After Soil Burial

Sample	Before soil burial			Weight loss (%)	After soil burial for 10 days		
	[Ester]/[Carbonate][a]	M_n[b] $\times 10^{-3}$	M_w/M_n[b]		[Ester]/[Carbonate][a]	M_n[b] $\times 10^{-3}$	M_w/M_n[b]
4a	100/0	20.6	1.9_5	16	100/0	15.0	2.8_1
4b	93/7	11.8	2.1_7	90	89/11	13.1	1.9_8
4c	82/18	12.0	1.9_3	20	78/22	9.8	2.6_6
4d	71/29	8.0	2.0_1	24	67/33	12.5	2.2_4
4e	51/49	11.5	2.4_6	3	50/50	16.5	2.1_8
4f	0/100	16.7	2.1_9	5	0/100	20.1	2.0_5

[a] Determined by ^{1}H-NMR.
[b] Determined by SEC in chloroform (polystyrene standard).

extracellular enzymes from microorganisms in the soil and that non-enzymatic hydrolysis is, if any, a minor degradation process. Figure 3 is an SEM photograph of the film of poly(ester carbonate) **4e** with the carbonate content of 49 mol % after the soil burial for 35 days, demonstrating that the film surface was eroded by actinomycetes.

Degradation in an activated sludge

BOD measurements were carried out on the poly(ester carbonate films in an activated sludge according to JIS K6950. The BOD biodegradability was evaluated as the percent of the consumed oxygen volume to the theoretical value necessary to oxidize the sample completely. The results are shown in Figure 4. Poly(ester carbonate)s **4a–4d** with a carbonate content of less than 30 mol % gradually degraded after an induction period of 1 week or so, and their BOD biodegradability increased to higher than 40% after 28 days. In sharp contrast, poly(ester carbonate) **4e** with a carbonate content of 49% scarcely degraded during the treatment in the activated sludge. Probably, under the conditions examined (25°C), poly(ester carbonate) **4e** is in the glassy state and lacks a conformational flexibility, so that the polymer chain cannot readily fit the active site of extracellular enzymes from microorganisms.

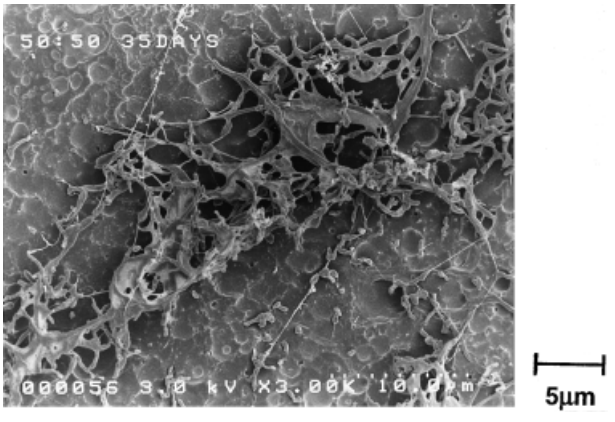


Figure 3 Scanning electron micrograph of poly(ester carbonate) **4e** recovered after soil burial for 35 days. Carbonate content of 49 mol %; film thickness, 200 μm; composted soil, pH 6.8; temperature, 27°C; humidity, 70–80%.

Figure 5 shows the BOD biodegradability of 1,4:3,6-dianhydro-2,5-bis-*O*-(methoxycarbonyl)-D-glucitol, a model compound of the polycarbonate, determined under the conditions similar to those for the degradation of the polymer films. The BOD degradability reached nearly 60% after 28 days, indicating that the carbonate structure involving a 1,4:3,6-dianhydro-D-glucitol moiety is susceptible to enzymatic degradation. The remarkable difference in the BOD degradability between polycarbonate **4f** and the model compound may arise chiefly from much less steric hindrance around the carbonate linkages of the latter.

Enzymatic degradation

Enzymatic degradation of poly(ester carbonate)s **4** was carried out in a phosphate buffer solution and monitored by TOC measurements of the solutions containing water-soluble degradation products. The TOC measurements were carried out three times on each combination of a sample and an enzyme, and the average value, corrected for the concurrent nonenzymatic hydrolysis, was represented as the TOC.

Five different enzymes were used for the measurements. *Candida rugosa* lipase and *Streptmyces rochei* carboxylate were scarcely effective or completely ineffective. *Pseudomonas sp.* lipoprotein lipase was effective for polyester **4a**, but much less effective for poly(ester carbonate)s **4b–4e**. Figure 6 presents the results on the enzymatic degradation using *Pseudomonas sp.* lipase. Except for poly(ester carbonate) **4e** with a carbonate content of 49 mol % and polycarbonate **4f**, the TOC values due to the enzymatic degradation are much higher than are the TOC values due to the nonenzymatic hydrolysis. Noteworthy is the finding that three poly(ester carbonate)s **4b–4d** with a carbonate content of less than 30 mol % showed higher TOC values than those of polyester **4a**. Similar results were obtained for the enzymatic degradation of poly(ester carbonate)s **4** using *Porcine pancreas* lipase. These re-

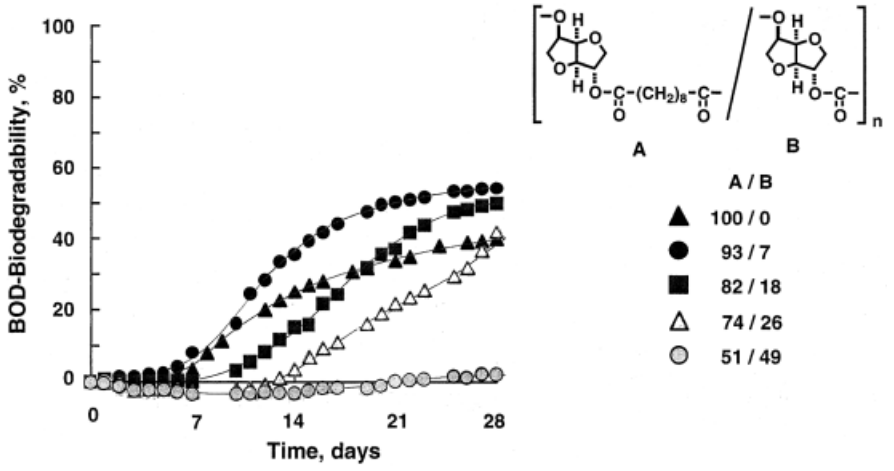


Figure 4 Biodegradation of poly(ester carbonate)s **4** in an activated sludge. Sample, 15 mg; activated sludge, 150 mL; temperature, 25°C.

sults are in accordance with the results on the soil burial degradation and the degradation in an activated sludge as described above.

Masuda et al. synthesized poly(ester carbonate)s from dimethyl succinate, diphenyl carbonate, and 1,4-butandiol and found that the enzymatic degradability as well as the degradability in soil were maximum for the poly(ester carbonate)s with a carbonate content of 20–40 mol %.[26] They correlated the enhanced biodegradability of these polymers with the decreased crystallinity of the samples. Yasuda et al. reported that the ε-caprolactone copolymer containing small amounts of 1-methyltrimethylene carbonate or 1,3-dimethyltrimethylene carbonate units showed high enzymatic degradation and high decomposition by activated sludge.[27] They also explained the fast biodegradation of the copolymers by the reduction of crystallinity compared to the corresponding polyester.

The aforementioned results of the biodegradability of poly(ester carbonate)s **4** can be only partly explained by the reduction of crystallinity, because all the poly(ester carbonate)s **4c–4f** with the carbonate content of 15 mol % and higher are amorphous. In addition to the effects of the crystallinity, the glass transition temperature and surface properties of the films should affect the enzymatic biodegradability. Poly(ester carbonate) **4e** and, in particular, polycarbonate **4f** have a glass transition temperature higher than the temperatures at which the three degradation experiments described above were carried out. These two polymers are in a glassy state at the experimental temperatures, and, hence, the effective binding of the enzyme is less likely to take place due to the lack of the flexibility of the polymer chain.

To shed light on the effect of the surface properties on the biodegradation, we measured contact angles of

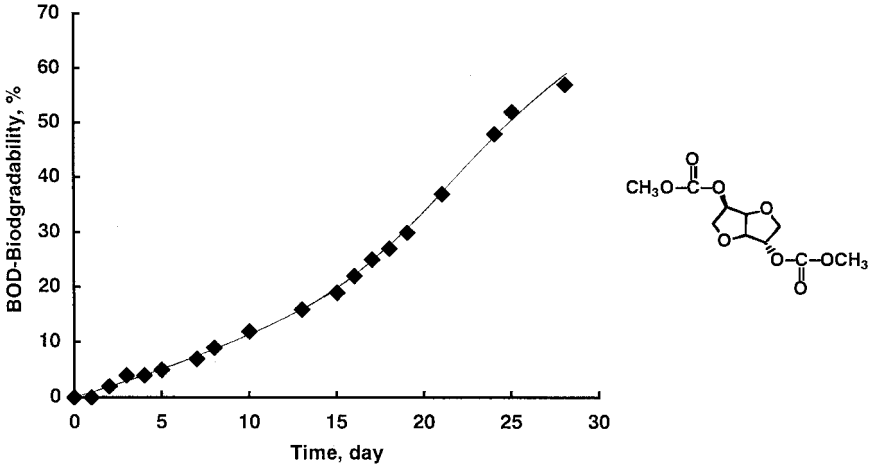


Figure 5 Biodegradation of 1,4:3,6-dianhydro-2,5-*O*-bis(methoxycarbonyl)-D-glucitol in an activated sludge. Sample, 10 mg; activated sludge, 150 mL; temperature, 25°C.

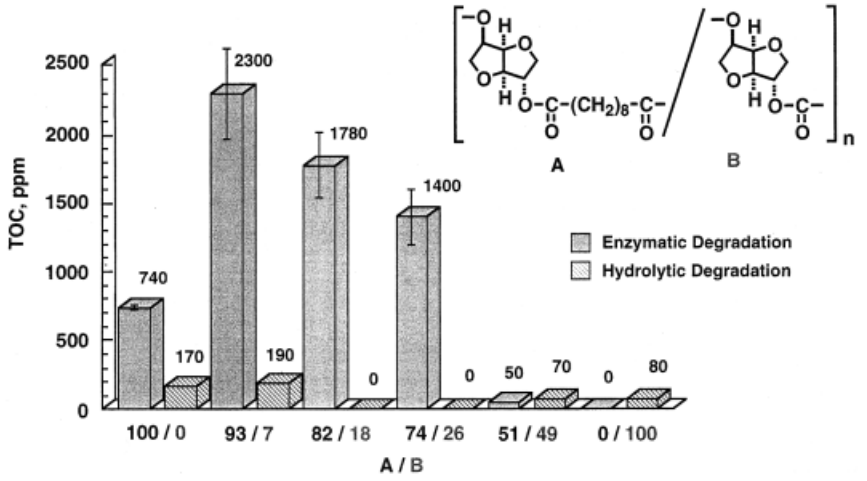


Figure 6 Enzymatic degradation of poly(ester carbonate)s **4** by *Pseudomonas sp.* lipase. Sample 25 mg; enzyme, 250 units; phosphate buffer, pH 7.0, 2 mL; incubated at 80 strokes/min at 37°C for 24 h.

water and diiodomethane on the surfaces of the polymer films. Table III presents the results of the measurements. The contact angles of both water and diiodomethane exhibited the maximum values for the poly(ester carbonate)s with a carbonate content of about 10–20 mol %. The measurements suggest that the surface of polycarbonate **4f** is of the highest hydrophilicity, whereas the surfaces of poly(ester carbonate)s **4b** and **4c** containing small amounts of the carbonate units are of the highest hydrophobicity. In general, degradation of polymers by lipase proceeds via two steps, namely, hydrophobic adsorption of the enzymes on the polymer surface as the first step, followed by the cleavage of the polymer chain by the active site of the adsorbed enzyme. The biodegradation data described above can be qualitatively correlated with the hydrophobicity of the film surface, that is, the higher the hydrophobicity of the surface, the higher is the biodegradability. The higher hydrophobicity of the film surface facilitates the adsorption of enzymes onto the surface, thus favoring the biodegradation.

TABLE III
Contact Angle and Surface Free Energy of Poly(ester carbonate) 4 Films[a]

Sample	[Ester]/ [Carbonate]	Contact angle (degree)		Free energy[b] (erg/cm^2)		
		Water	CH_2I_2	γ_s^d	γ_s^p	γ_s
4a	100/0	87	36	40.5	1.0	41.5
4b	93/7	94	41	38.5	0.5	39.0
4c	82/18	90	49	33.4	1.7	35.1
4d	74/26	81	44	34.4	4.1	38.5
4e	51/49	75	38	36.6	6.0	42.6
4f	0/100	74	38	36.4	6.6	43.0

[a] Prepared by the solvent-cast method from chloroform on a polytetrafluoroethylene plate.

[b] Calculated by the Owens' method: γ_s^d denotes dispersion force component of solid surface free energy and γ_s^p denotes polar force component of solid surface free energy.

The surface free energies of these polymer films were estimated from the measurements of the contact angles of water and diiodomethane using Owens' method.[35] The total surface free energy is the lowest for poly(ester carbonate) **4c** with a carbonate content of 18%. The data of the contact angle of water in combination with the biodegradability described above suggest that poly(ester carbonate)s **4** with a lower surface free energy are more readily degraded by the action of enzymes. From the data in Table III, it appears that the less degradable polymers have a somewhat larger proportion of the polar force component of the surface free energy, although the proportion of the dispersion force component is overwhelmingly higher. In the present case, hydrogen bonding is responsible mainly for the polar force component of the surface free energy. Thus, it seems likely that hydrogen bonding on the film surface hinders the hydrophobic adsorption of the enzyme on the surface, thus disfavoring the biodegradation.

As we pointed out in the section on the degradation in an activated sludge, the carbonate linkage involving a 1,4:3,6-dianhydro-D-glucitol unit is potentially susceptible to enzymatic degradation. However, the carbonate linkage in polycarbonate **4** is inserted between two bulky and rather stiff 1,4:3,6-dianhydro-D-glucitol units and, hence, the approach of the active site of enzymes to the carbonate linkage is severely hindered. We examined the enzymatic degradation of a low molecular weight polycarbonate **4f** (M_n 2.6 $\times$ 10^3) using different enzymes (*Porcine pancreas* lipase, *Porcine liver* esterase, *Pseudomonas sp.* lipase, *Pseudomonas sp.* cholesterol esterase, *Pseudomonas sp.* lipoprotein lipase, proteinase K, and papain). Among the seven enzymes examined, only papain was appreciably ef-

fective, the TOC value being 410 ppm under the same conditions as shown in the legend of Figure 6. The TOC values for the other enzymes were less than 150 ppm. The enzymatic degradability of the polycarbonate samples showed a tendency to decrease with the increase in the molecular weight of the polycarbonate. The TOC values decreased to 320 and 240 ppm for the polycarbonate samples with M_n 5.8 $\times$ 10^3 and 16.7 $\times$ 10^3, respectively. These data demonstrate that the polycarbonate moiety containing 1,4:3,6-dianhydro-D-glucitol units is intrinsically biodegradable.

CONCLUSIONS

Poly(ester carbonate)s **4** with different compositions were synthesized by bulk polycondensation of 1,4:3,6-dianhydrro-D-glucitol (**1**) with diphenyl sebacate and diphenyl carbonate. The soil burial degradation tests of the films of **4**, the BOD measurements in an activated sludge, and the enzymatic degradation tests using several enzymes led us to conclude that poly(ester carbonate)s **4** are potentially biodegradable. The biodegradability depends on the carbonate content, being highest for poly(ester carbonate)s with a carbonate content of about 10–20 mol % and it decreases markedly for poly(ester carbonate)s with the carbonate content of about 50 mol % or higher. The high molecular weight polycarbonate **4f** is reluctant to undergo enzymatic hydrolysis by lipases, but the low molecular weight polycarbonates are degraded, although very slowly, by the action of papain.

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