Effects of Geometrical Difference of Unsaturated Aliphatic Polyesters on Their Biodegradability III.   Cross Effects of Molecular Weight and Geometric Structure of Poly(ethylene maleate/fumarate) and Its Model Compounds

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ABSTRACT: Unsaturated polyesters, **P1a** and **P2a**, having different molecular weight were synthesized by solution polycondensation of maleic anhydride (MAn) with ethylene glycol (EG). Furthermore, unsaturated polyesters, poly(ethylene maleate/fumarate) (**P1b-e** and **P2b-e**), which have various ratios of different *Z-/E*-configuration at the C=C double bond were readily delivered from **P1a** and **P2a**, respectively, in 1,2-dichloroethane by using morpholine as a catalyst for isomerization.   In order to discuss separately the effects of molecular weight of the samples on their biodegradability from the effects due to configuration of C=C double bond, several *Z*- or *E*-rich oligomeric model compounds having methyl esters as the terminal groups were prepared.   The biodegradability of these polyester samples and oligomeric model compounds was evaluated from biochemical oxygen demand (BOD) values in the presence of an activated sludge.   As the number-average molecular weight of both oligomeric model compounds and unsaturated polyesters was higher, their biodegradability was lowered by introducing C=C double bond, especially, by that of *Z*-configuration.

KEY WORDS   Biodegradability / Unsaturated Polyester / Geometrical Isomer / Polycondensation / Maleic Anhydride / Ethylene Glycol /

Synthetic polymeric materials have provided many advantages in our daily life for the last century, and become one of the most important materials.   When once synthetic polymeric materials are disposed, however, those often caused serious environmental problems.   Thus biodegradable polymers which were completely decomposed to CO_2 and H_2O in nature have received much attention in recent years as one of the answers to solve the problems.   In fact, biodegradable polymers, especially aliphatic polyesters, have been widely investigated by many scientists in the world.

In spite of a large number of studies on biodegradability of polyesters, little attention has been given to unsaturated polyesters.[1—7]   Tokiwa and Suzuki reported that a few unsaturated polyesters containing 2-butenediol unit could be hydrolyzed by lipase.[1]   On the other hand, slightly cross-linked unsaturated polyesters, poly(hexamethylene fumarate) and poly(*cis*-2-butene fumarate), were hardly hydrolyzed by lipase.

A carbon–carbon double bond in unsaturated polyesters has two geometrical isomers (*Z*- and *E*-configuration) and such difference should affect their biodegradability depending on the substrate specificity of enzyme.   In controlling the biodegradation rate of polyester, it must be useful to make geometrical effects clear.   In our previous paper,[6, 7] it was shown that in comparison with saturated polyesters, the ef-

ficient degradation was prevented by introducing *Z*-configuration of C=C double bond in the polyesters but introducing *E*-configuration did not do so remarkably.   In addition to biochemical oxygen demand (BOD) measurement of polymer samples, dimethyl esters derived from the corresponding acids, maleic and fumaric acid, were measured.   It was revealed that the simplest dimethyl esters are essentially subject to biodegradation even though it contains C=C double bond.   As the chain length of polyester having the double bond was longer, its biodegradability seemed to become lower.   The biodegradation rate of unsaturated polyesters might be influenced by chain length of the polyesters as well as molar fractions of *Z-/E*-configuration at C=C double bond. Polymer samples in our previous works, oligomeric components less than about 1000 of their molecular weights were removed during purification by reprecipitation. It was very important for the present work to ensure the variety of samples in an oligomer region, otherwise we had only dimethyl maleate (or fumarate) as a model compound. Making a comparison between the polymers with only dimethyl maleate (or fumarate) did not give so fruitful information.   Therefore we have been required to improve a preparative method for such oligomeric samples instead of polymerization route.

In this paper, in order to make clarify the effects of chain length of the unsaturated polyesters on their biodegradability, *Z*-rich oligomeric model compounds

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Z1-4 with different chain length were prepared from maleic anhydride (MAn) with ethylene glycol (EG). Furthermore, *E*-rich oligomeric model compounds **E1-4** were prepared through isomerization of the model compounds **Z1-4** in 1,2-dichloroethane (DCE) by using morpholine (Mor) as a catalyst.[7,8] Unsaturated polyesters **P1a** and **P2a** were synthesized by solution polycondensation of MAn with EG in the presence of *p*-toluenesulfonic acid (*p*-TsOH) as a catalyst. Unsaturated polyesters **P1a** (M_n = 1.3 × 10³) and **P2a** (M_n = 3.5 × 10³) were also isomerized to give the polyesters **P1b-e** and **P2b-e** which have a various ratios of different *Z*-/*E*-configuration at the C=C double bond in a similar manner as preparation of oligomeric model compounds. The biodegradability of oligomeric model compounds and polyesters was evaluated from BOD values in an activated sludge. Thus, we would be able to discuss separately the effects of a chain length of unsaturated polyesters on their biodegradability from that due to configuration at C=C double bond.

EXPERIMENTAL

Materials

Maleic anhydride (MAn), maleic acid (MA), fumaric acid (FA), ethylene glycol (EG), *p*-toluenesulfonic acid (*p*-TsOH), and morpholine (Mor) were purchased from Nacalai Tesque, Inc., Kyoto, Japan. MAn was purified by recrystallization from chloroform. EG, toluene (Tol), 1,2-dichloroethane (DCE), and Mor were purified by distillation according to conventional methods before use. For generation of diazomethane, a mixture of 100 mL of diethyl ether and 30 mL of 40% aqueous potassium hydroxide in a long glass tube was cooled to keep under 0 °C, 10 g of powdered nitrosomethylurea was added in portions with shaking, and the yellow diazomethane in diethyl ether was separated by decantation. Nitrosomethylurea is synthesized from methylamine hydrochloride, urea, and sodium nitrite.[9]

Measurement

FT-IR spectra were recorded for film samples cast on KBr disk from chloroform solutions, using a JASCO FT/IR-430 spectrometer. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 27 °C using a Bruker DPX-200 MHz spectrometer. All of the chemical shifts were expressed as δ downfield from tetramethylsilane (TMS). The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of polymers were determined at 40 °C by gel permeation chromatography (GPC) calibrated with polystyrene standards using a system of Tosoh HLC-8020 equipped with a Tosoh RI-8020 detector and Tosoh G2000-HXL, G3000-HXL, G4000-HXL, and G5000-HXL columns. Tetrahydrofuran was used as an eluent. Glass transition temperature (T_g) of the samples were determined by differential scanning calorimetry (DSC) using a Seiko Instrument DSC 210 from −100 to 120 °C at a heating rate of 10 °C min⁻¹.

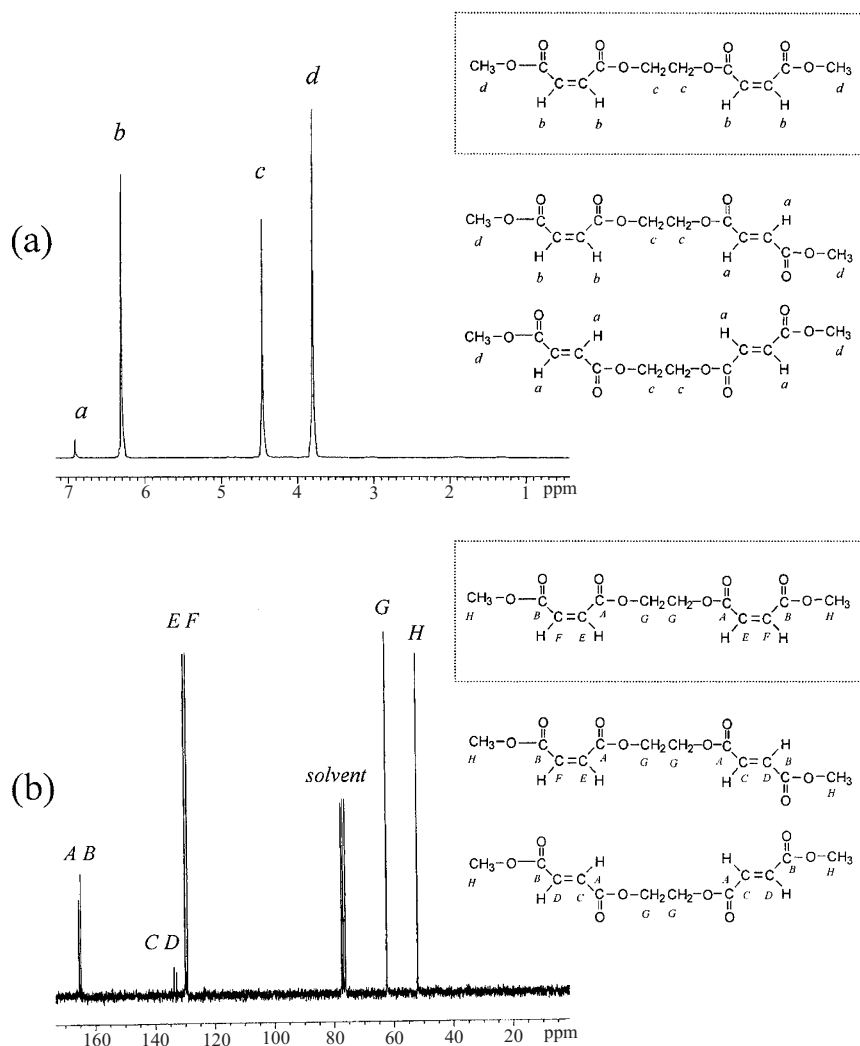### Synthesis of Z-rich Oligomeric Model Compounds

MAn (2.45 g, 25 mmol) was placed into a 50 mL round-bottomed flask equipped with a magnetic stirrer and a nitrogen gas inlet. The flask was immediately immersed in an oil bath and heated up to 120 °C. After MAn had been melted, EG (1.55 g, 25 mmol) was added, and the mixture began first step reaction at 120 °C. Water produced during the first step reaction was removed under a reduced pressure (0.2 mmHg). After prescribed time (6–24 h), excess MAn (22.06 g, 225 mmol) was added and allowed to react moreover 3 h at nitrogen atmosphere as second step reaction. In the case of **Z1**, all MAn (24.52 g, 250 mmol) was added before second step reaction. After cooling down to room temperature, the mixture was diluted with CHCl₃, and added dropwise cold solution of diazomethane in diethyl ether. The organic layer was washed with 5% NaHCO₃ and dried over MgSO₄. Evaporation of solvent gave *Z*-rich model compounds: Yield; 1.21 g (16.9%), for model compound **Z1**, the others **Z2-Z4** are 1.01 g, 0.86 g, and 1.32 g, respectively. IR of **Z1** (KBr disk, cm⁻¹): 2956 [ν_{C-H}], 1730 [$\nu_{C=O}$ (ester)], 1643 [$\nu_{C=C}$], and 1160 [ν_{C-O-C} (ester)]. ¹H NMR of **Z1** (CDCl₃, δ ppm): 6.89 [C*H*=C*H*(*E*-configuration)], 6.29 [C*H*=C*H* (*Z*-configuration)], 4.46 [OC*H*₂C*H*₂O], and 3.80 [COOC*H*₃]. ¹³C NMR of **Z1** (CDCl₃, δ ppm): 165.4 [CH=CH*C*OOCH₂CH₂–], 164.8 [CH=CH*C*OOCH₃], 133.8 [CH=*C*HCOOCH₂CH₂–(*E*-configuration)], 133.0 [CH=*C*HCOOCH₃ (*E*-configuration)], 130.1 [CH=*C*HCOOCH₂CH₂–(*Z*-configuration)], 129.3 [CH=*C*HCOOCH₃ (*Z*-configuration)], 62.5 [O*C*H₂*C*H₂O], and 52.1 [COO*C*H₃]. *Z*-/*E*-configuration molar ratio of **Z1** was 93/7, the others **Z2-4** are in Table I, determined by the intensity of ratio of peak *b*/*a* shown in Figure 1a.

Table I. Characteristics of *Z*-rich model compounds (**Z1-4**)[a]

Model compound *Z*-series	Reaction time (h)	Z/E[b]	M_n[c] × 10⁻²	M_w/M_n[c]	T_g[d] (°C)
Z1	0 + 3	93 / 7	2.8	1.1	−61.6
Z2	6 + 3	75 / 25	5.7	1.8	−56.0
Z3	12 + 3	76 / 24	6.7	1.9	−54.1
Z4	24 + 3	67 / 33	10.4	2.0	−53.6

[a]See text of experimental part; reaction temperature = 120 °C. [b]Molar ratio of *Z*- and *E*-conformation unit in polymer, determined by ¹H NMR. [c]Determined by GPC calculated by polystyrene standards; eluent, THF. [d]Determined by DSC; heating rate, 10 °C min⁻¹.

Figure 1. NMR spectra of Z-rich model compound **Z1** in CDCl₃ at 27 °C; (a) ¹H NMR, (b) ¹³C NMR.

Isomerization Reaction of Z-rich Oligomeric Model Compounds

A typical experimental procedure is as follows. *Z*-rich model compounds **Z1** (0.26 g, 1.0 mmol) was placed into a 10 mL round-bottomed flask equipped with reflux condenser, dissolved completely in 2.0 mL of DCE at room temperature under the nitrogen atmosphere. After Mor (0.01 g, 0.1 mmol) had been added, the flask was immersed in an oil bath and immediately heated up to 80 °C. The mixture was stirred by magnetic stirrer at 80 °C for 120 min. After cooling down to room temperature, the mixture was diluted with CHCl₃, and washed with water three times. The organic layer was dried *in vacuo* at room temperature to give *E*-rich model compounds **E1**: Yield; 0.177 g, 68.5%, for the model compound **E1**, the others **E2-E4** are in Table II. IR of **E1** (KBr disk, cm⁻¹): 2963 [ν_{C-H}], 1719 [$\nu_{C=O}$ (ester)], 1647 [$\nu_{C=C}$], and 1153 [ν_{C-O-C} (ester)]. ¹H NMR of **E1** (CDCl₃, δ ppm): 6.88 [CH=CH(*E*-configuration)],

Table II. Isomerization reaction of **Z1-4** to *E*-rich model compounds (**E1-4**) in the presence of Mor[a]

Model compound *E*-series	Yield g(%)	Z/E[b]	M_n[c] $\times 10^{-2}$	M_w/M_n[c]	T_g[d] (°C)
E1	0.18 (68.5)	1 / 99	2.8	1.1	−41.6
E2	0.14 (55.5)	2 / 98	6.0	1.7	−37.5
E3	0.17 (65.2)	1 / 99	7.4	1.7	−33.7
E4	0.15 (58.1)	1 / 99	10.6	1.9	−29.9

[a]**Z1-4** = 0.26 g (1.0 mmol); Mor = 0.01 g (0.1 mmol); DCE = 2.0 mL; reaction temperature = 80 °C; reaction time = 120 min. [b]Molar ratio of *Z*- and *E*-conformation unit in polymer, determined by ¹H NMR. [c]Determined by GPC calculated by polystyrene standards; eluent, THF. [d]Determined by DSC; heating rate, 10 °C min⁻¹.

6.28 [CH=CH(*Z*-configuration)], 4.47 [OCH_2CH_2O], and 3.82 [COOCH_3]. ¹³C NMR of **E1** (CDCl₃, δ ppm): 165.1 [CH=CHCOOCH₂CH₂–], 164.5 [CH=CHCOOCH₃], 134.0 [CH=CHCOOCH₂CH₂– (*E*-configuration)], 132.9 [CH=CHCOOCH₃ (*E*-configuration)], 62.7 [OCH₂CH₂O], and 52.3 [COOCH₃]. *Z*-/*E*-configuration molar ratio of **E1** was 1/99, the others **E2-4** are in Table II.

Table III. Solution polycondensation of MAn with EG catalyzed with *p*-TsOH[a]

Polyester	*p*-TsOH (mol%)	Yield (%)	Z/E[b]	M_n[c] $\times 10^{-3}$	M_w/M_n[c]	m_1/m_2[d]
P1a	0.1	79.8	78 / 22	1.3	1.5	44/ 56
P2a	1.0	87.6	81 / 19	3.5	1.5	46/ 54

[a]$[MAn]_0 = [EG]_0 = 100.0$ mmol; $[Tol]_0 = 50$ mL; reaction temp = 130 °C; reaction time = 24 h. [b]Molar ratio of *Z*- and *E*-conformation unit in polymer, determined by ^{1}H NMR. [c]Determined by GPC calculated by polystyrene standards; eluent, THF. [d]Molar ratio of MAn (m_1) unit to EG (m_2) unit in polymer, determined by ^{1}H NMR.

Table IV. Isomerization reaction from *Z*- to *E*-configuration for polyester **P1a** and **P2a** in the presence of Mor[a]

Polyester	Reaction Time (min)	Yield g (%)	Z/E[d]	M_n[e] $\times 10^{-3}$	M_w/M_n[e]	T_g[f] (°C)
P1a	–	–	78 / 22	1.3	1.5	−38.7
P1b[b]	10	0.59 (82.5)	49 / 51	1.4	1.4	−18.5
P1c[b]	30	0.59 (83.4)	38 / 62	1.4	1.4	−14.0
P1d[b]	60	0.53 (74.1)	18 / 82	1.5	1.5	−10.2
P1e[b]	120	0.50 (71.0)	5 / 95	1.5	1.5	− 0.4
P2a	–	–	81 / 19	3.5	1.5	−17.5
P2b[c]	10	0.53 (74.9)	50 / 50	3.7	1.6	−14.7
P2c[c]	30	0.56 (79.3)	29 / 71	4.0	1.6	− 9.7
P2d[c]	60	0.46 (64.9)	12 / 88	4.2	1.6	− 7.0
P2e[c]	120	0.51 (72.3)	9 / 91	4.1	1.6	− 6.3

[a]Polyester **P1a** or **P2a** = 0.71 g (5.0 mmol); DCE = 10.0 mL; reaction temperature = 80 °C. [b]Mor = 0.08 g (1.0 mmol). [c]Mor = 0.04 g (0.5 mmol). [d]Molar ratio of *Z*- and *E*-conformation unit in polymer, determined by ^{1}H NMR. [e]Determined by GPC calculated by polystyrene standards; eluent, THF. [f]Determined by DSC; heating rate, 10 °C min^{−1}.

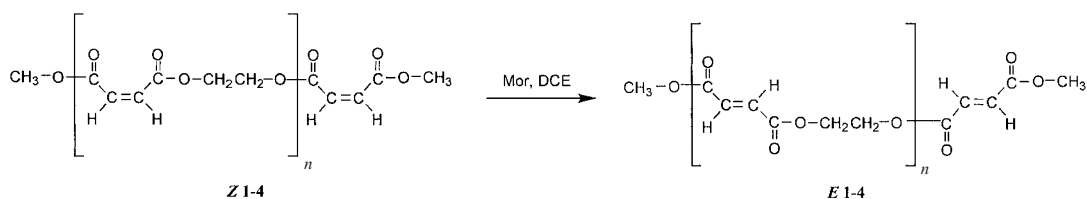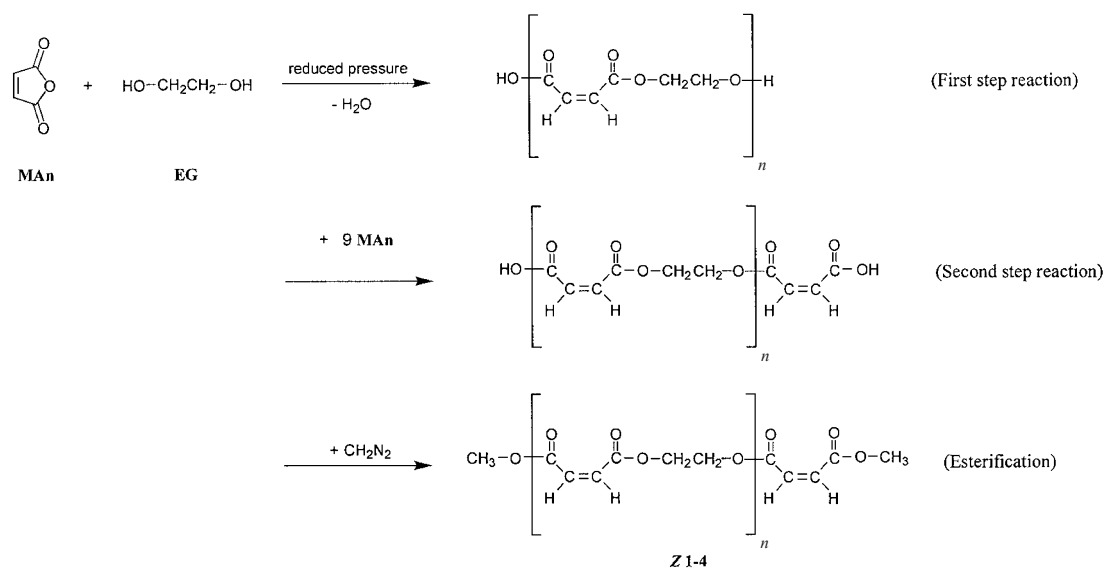## *Polycondensation of Maleic Anhydride with Ethylene Glycol*

Unsaturated polyesters **P1a** and **P2a** were prepared by a solution polycondensation method.[10−13] A typical experimental procedure is as follows. MAn (9.81 g, 100.0 mmol), EG (6.21 g, 100.0 mmol), Tol (50.0 mL), and the required amount of *p*-TsOH as a catalyst were placed into a 100 mL round-bottomed flask equipped with a Dean–Stark trap with a reflux condenser, and a nitrogen gas inlet. The reaction mixture was refluxed at 130 °C for 24 h under a stream of nitrogen, stirring magnetically. After cooling, the mixture was diluted with CHCl$_3$, and then the organic solution was poured into diethyl ether to obtain precipitate. After reprecipitation from CHCl$_3$ solution into diethyl ether three times, the polymeric materials were collected and dried *in vacuo* at room temperature to give polyester **P1a**: Yield; 11.3 g (79.8%) for **P1a** and 12.5 g (87.6%) for **P2a** in Table III. IR of **P1a** (KBr disk, cm^{-1}): 2961 [ν_{C-H}], 1735 [$\nu_{C=O}$ (ester)], 1643 [$\nu_{C=C}$], and 1162 [ν_{C-O-C} (ester)]. ^{1}H NMR of **P1a** (CDCl$_3$, δ ppm): 6.89 [C*H*=C*H*(*E*-configuration)], 6.31 [C*H*=C*H*(*Z*-configuration)], and 4.42 [OC*H$_2$*C*H$_2$*O]. ^{13}C NMR of **P1a** (CDCl$_3$, δ ppm): 164.7 [*C*O], 133.5 [*C*H=*C*H (*E*-configuration)], 129.8 [*C*H=*C*H (*Z*-configuration)], and 62.6 [O*C*H$_2$*C*H$_2$O]. *Z/E* ratio was found as 78/22 for **P1a** and 81/19 for **P2a**, respectively.

Isomerization Reaction of Polyesters P1a and P2a

Isomerization reaction of polyesters **P1a** and **P2a** carried out in a similar manner to that of the model compounds described above. Polyesters **P1b-e** and **P2b-e** were purified by reprecipitation of CHCl$_3$ solution into diethyl ether: Yield; 0.59 g, 82.5%, for polyester **P1b**, the others are in Table IV. IR of **P1b** (KBr disk, cm^{-1}): 2959 [ν_{C-H}], 1725 [$\nu_{C=O}$ (ester)], 1643 [$\nu_{C=C}$], and 1158 [ν_{C-O-C} (ester)]. ^{1}H NMR of **P1b** (CDCl$_3$, δ ppm): 6.89 [C*H*=C*H*(*E*-configuration)], 6.30 [C*H*=C*H*(*Z*-configuration)], and 4.43 [OC*H$_2$*C*H$_2$*O]. ^{13}C NMR of **P1b** (CDCl$_3$, δ ppm): 164.5 [*C*O], 133.6 [*C*H=*C*H (*E*-configuration)], 129.9 [*C*H=*C*H (*Z*-configuration)], and 62.8 [O*C*H$_2$*C*H$_2$O]. *Z/E* ratio was summarized in Table IV.

Biochemical Oxygen Demand Test

Biochemical oxygen demand (BOD) value of the samples was determined by the oxygen consumption method according to the JIS K 6950 in aerobic at 25 °C, using a BOD tester (Model 200F, TAITEC Co., Koshigaya, Japan). The activated sludge was available from Municipal disposal plant in Nagoya. The incubation medium was composed of K$_2$HPO$_4$ (217.5), KH$_2$PO$_4$ (85.0), Na$_2$HPO$_4$·2H$_2$O (334.0), NH$_4$Cl (5.0), CaCl$_2$·2H$_2$O (36.4), MgSO$_4$·7H$_2$O (22.5), FeCl$_3$·6H$_2$O (0.25 mg L^{-1}), kept at pH =

Scheme 1. Synthesis of *Z*-rich oligomeric model compounds (**Z1-4**).

Scheme 2. Isomerization of *Z*-rich oligomeric model compounds (**Z1-4**).

7.4 ± 0.1. Since polyester samples and oligomeric model compounds were viscous liquid at room temperature, each sample in chloroform solution was cast to film on bottom of the bottle in height of 2 cm. Corresponding simplest monomer unit, MA, FA (powder), and EG (liquid) were added to bottom of the bottle as it is. The concentration of polymers in the incubation medium was $100 \, mg \, L^{-1}$.

RESULTS AND DISCUSSION

Synthesis of Z-rich Oligomeric Model Compounds

According to Scheme 1, *Z*-rich oligomeric model compounds **Z1-4** were prepared from MAn with EG at 120 °C. Melt polycondensation under reduce pressure was carried out at the first step reaction. As the first step reaction time became longer, the chain length of the oligomeric model compounds was also longer. At the second step reaction, excess MAn was subjected to react with terminal hydroxyl groups of oligomers. Almost end groups of the model compounds could be completely converted to carboxyl groups, judging from spectroscopic data after dealing with CH_2N_2. After cooling, the reaction solution was diluted with $CHCl_3$ and then cold solution of diazomethane in diethyl ether was added dropwise. Carboxyl end groups in the model compounds could be immediately changed to methyl ester groups at room temperature. In the synthesis of *Z*-rich oligomeric model compounds **Z1-4**, light-brown viscous sample showing no T_m was obtained (Table I).

The NMR spectra for **Z1** are shown in Figure 1. **Z1** was found to be dimethyl ester of almost single product consisted of MAn/EG = 2/1. However the others (**Z2-4**) were mixtures of a few oligomeric ester compounds, which confirmed by GPC. Molecular weights of **Z1-4** could be controlled in the region of the number-average molecular weight (M_n) from 2.8 to 10.4×10^2 by reaction time of the first step reaction. Although there were a few small peaks assigned to *E*-configuration at C=C double bonds in the NMR spectra for **Z1**, but **Z1** were mainly consisted of *Z*, *Z*-configuration compound. As the reaction time of the first step reaction was longer, isomerization from *Z*- to *E*-configuration at unsaturated acid units occurred partially as a result of long heating.

Isomerization Reaction of Z-rich Oligomeric Model Compounds

It is well known that the C=C double bond of *Z*-configuration can be more efficiently isomerized into *E*-configuration in the presence of amine compounds as a catalyst.[7, 8] Thus isomerization of *Z*-rich oligomeric model compounds **Z1-4** was examined with Mor in DCE at 80 °C (Scheme 2 and Figure 2). The NMR spectra for **E1** are shown in Figure 2. The occurrence
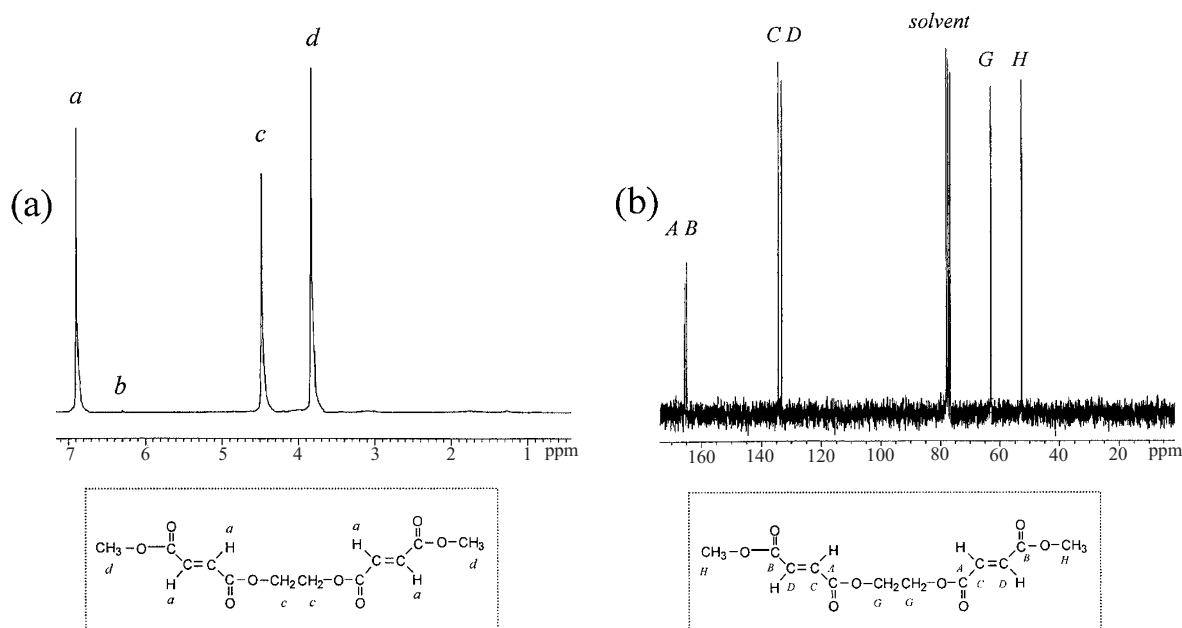
Figure 2. NMR spectra of E-rich model compound $E1$ in CDCl$_3$ at 27 °C; (a) ^{1}H NMR, (b) ^{13}C NMR.
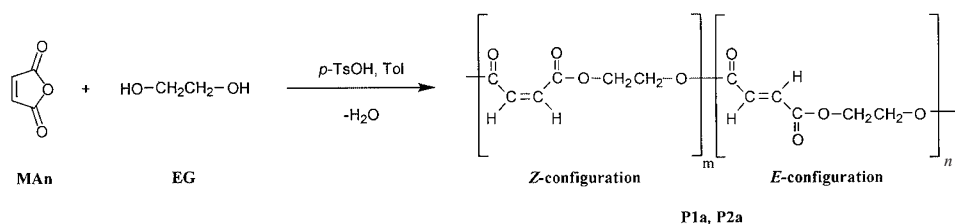
Scheme 3. Solution polycondensation of MAn with EG.

of isomerization from Z- to E-configuration was clearly confirmed by disappearance of peak b at about 6.3 ppm in Figure 2a and peak E and F at about 130 ppm in Figure 2b, which peaks are assigned to CH=CH (Z-configuration). The results are summarized in Table II, showing that highly E-rich oligomeric model compounds $E1$-**4** can be obtained without any remarkable change of molecular weight.

Solution Polycondensation of Maleic Anhydride with Ethylene Glycol

Soluble polyesters containing an unsaturated unit in organic solvents could not be achieved well through a melt polycondensation method because of gelation at the initial stage. Therefore solution polycondensation shown in Scheme 3 was employed to prepare unsaturated polyesters **P1a** and **P2a**.[10–13] Table III shows the results of solution polycondensation of MAn with EG.

M_n of polyesters **P1a** and **P2a** was 1.3×10^3 and 3.5×10^3, respectively, depended on quantity of p-TsOH. The unsaturated polyesters obtained by solution polycondensation were essentially a linear polymer, but their molecular weight could not be achieved to $M_n > 10^4$. To obtain polyester with higher molec-

ular weight, the chain extension reaction of polymers with a titanium isopropoxide catalyst was also examined previously.[14, 15] However it resulted in serious gelation of the polymer rather than the chain extension. For the present, it is difficult to obtain the unsaturated polyesters with high molecular weight without cross-linking. Thus, oligomeric polyester samples were suited for the biodegradation tests in order to discuss the geometrical effects on biodegradability of unsaturated polyesters without negative effects due to cross-linking.

It is also well known that the C=C double bonds of Z-configuration often isomerize into E-configuration during esterification of unsaturated anhydrides with diols in the presence of an acid catalyst.[16–19] The molar ratio of Z/E in polyesters **P1a** and **P2a** was 78/22 and 81/19, respectively. Since EG take place etherification with a stronger acid catalyst, formation of EG-EG linkage might not be removed completely in the course of the present polymerization. However, the composition ratio m_1/m_2 of **P1a** and **P2a** was nearly 1:1 composition and the content of ether units could be recognized as extremely low.
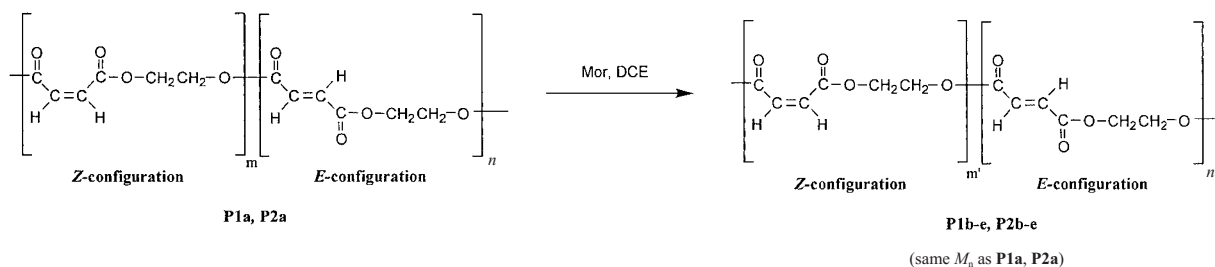
Scheme 4. Isomerization of polyesters **P1a** and **P2a**.

*Isomerization Reaction of Polyesters **P1a** and **P2a***

Isomerization reaction from *Z*- to *E*-configuration of polyesters **P1a** and **P2a** in DCE in the presence of Mor was also conducted (Scheme 4). The results are summarized in Table IV.

In comparison with **P2b-e**, isomerization reaction of **P1a** required the twice amount of Mor catalyst in order to obtain highly *E*-rich polyesters. It may be a reason that there is strong interaction between Mor and terminal carboxyl groups. Thus two series of unsaturated polyesters, **P1b-e** and **P2b-e** having the same molecular weight but the different ratio of *Z*-/*E*-configuration, could be optionally prepared from one original polymer **P1a** or **P2a** by controlling isomerization reaction time. The variety of *Z/E* values was wide enough to investigate geometrical effects on biodegradability.

Biochemical Oxygen Demand Test

The biodegradability of unsaturated polyesters and oligomeric model compounds was evaluated from BOD/TOD (TOD: theoretical oxygen demand) values measured with a BOD tester using the oxygen consumption method for 30 d in the presence of activated sludge. In addition to these samples, BOD values of MA and FA, and EG were also measured taking into account the biodegradability of the smallest repeating unit.

Figure 3 shows the BOD/TOD values against reaction times. Low molecular weight compounds, MA, FA, and EG, began to degrade immediately and its BOD/TOD values reached over up to 70% after 10 d. It could be concluded that monomer units supplied by hydrolysis of unsaturated polyesters are essentially biodegraded to CO_2 and H_2O by microorganism.

The biodegradability of oligomeric model compounds is shown in Figure 4. Even though two ester linkages were included in the same manner, the induction period of **Z1** was longer than that of **E1**. This is a basic evidence for that a microorganism might to distinguish differences of configuration at C=C double bond through hydrolysis and an aerobic metabolism process. In comparison with **Z1** and **E1**, every oligomeric


○: MA
□: FA
×: EG
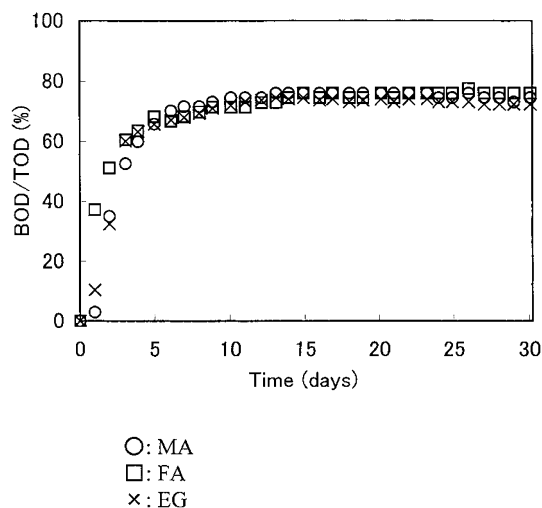
Figure 3. Biodegradability of MA, FA, and EG, corresponding to repeating units evaluated by biochemical oxygen demand (BOD) test.

model compounds, **Z2-4** and **E2-4**, resulted in the lower biodegradability. These results would be reflected by the increase of hydrophobicity of the samples. The BOD/TOD values of **E2-4** were somewhat smaller than that of **Z2-4** within 15 d. It is worth noting that the T_g values of **E2-4** were more about 20 °C higher than these of **Z2-4**. It may be reflected to the samples crystallinity on its biodegradability. Between **Z2** and **E2**, as well as **Z3** and **E3**, there were not significant effects of configuration on their biodegradability at 30 d. On the other hand, the values of BOD/TOD after 30 d for **Z4** and **E4**, which have rather high molecular weight, were 28.6% (**Z4**) and 41.9% (**E4**). This fact suggested that the preferential biodegradation with *E*-configuration could come out distinctly only when the molecular weight (M_n) of dimethylester model compounds was more than *ca.* 1000.

Figure 5 shows the BOD/TOD values *vs.* time diagram for unsaturated polyesters **P1a-e** ($M_n = 1.3$–1.5×10^3) and **P2a-e** ($M_n = 3.5$–4.2×10^3). In our previous paper,[6] it have already been revealed that the biodegradation of the correspond saturated aliphatic polyester, namely poly(ethylene succinate) [$M_n = 0.45$–2.05×10^4], could proceed immediately and did not so influenced by their molecular weight. In
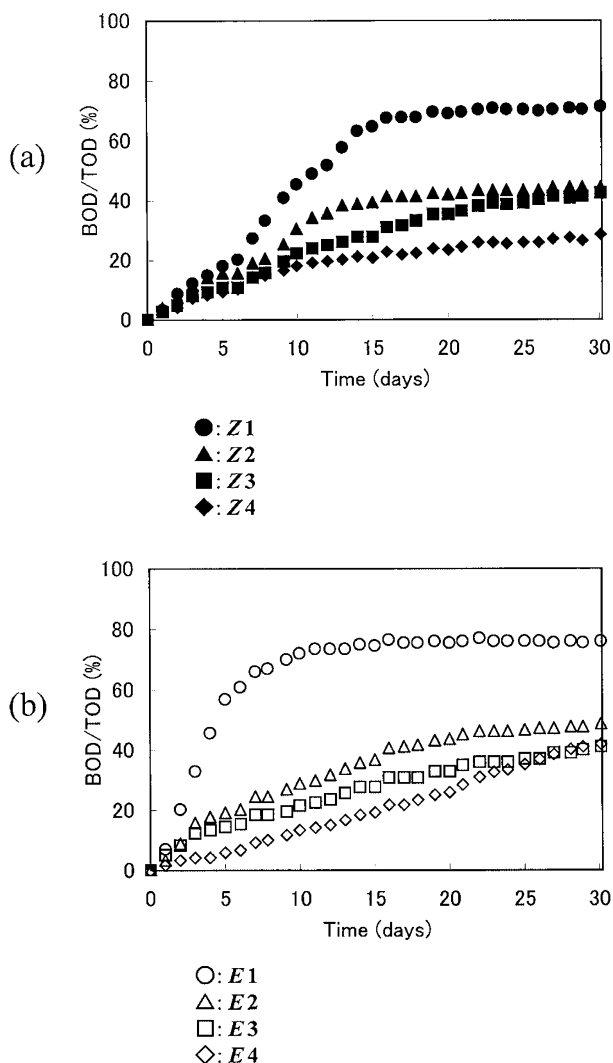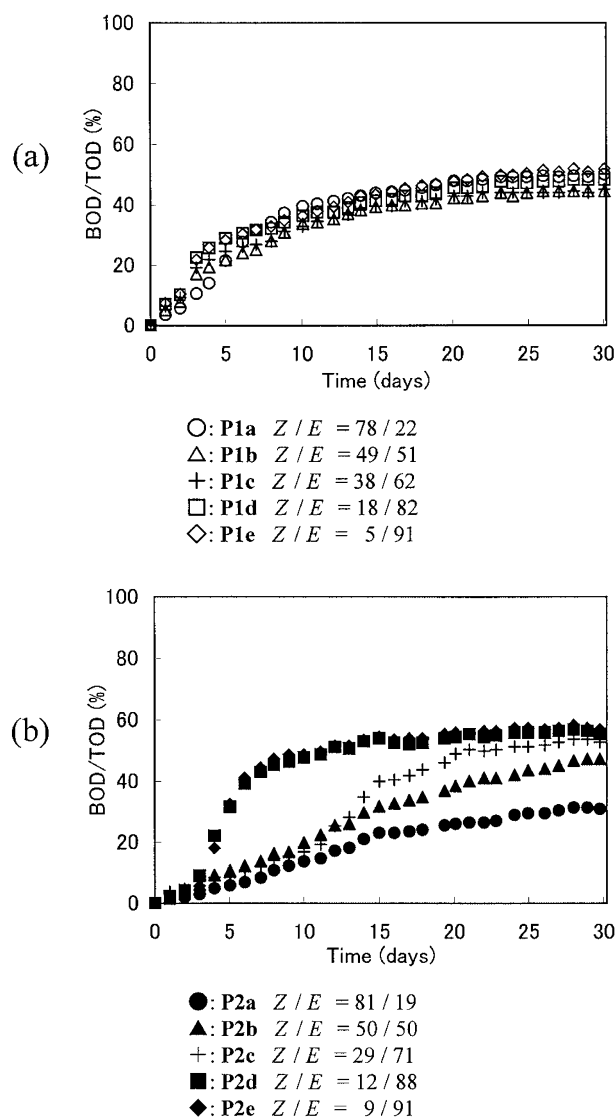
Figure 4. Biodegradability of oligomeric model compounds evaluated by BOD test; (a) *Z*-rich model compounds *Z*1-4, (b) *E*-rich model compounds *E*1-4.

Figure 5. Biodegradability of polyesters prepared from MAn and EG evaluated by BOD test; (a) **P1a-e**, (b) **P2a-e**.

comparison with the saturated polyesters, unsaturated polyesters **P1a-e**, which number average molecular weights were in range of $1.3–1.5 \times 10^3$, prevented their efficient biodegradation. It might be significantly influenced on their biodegradation that the flexibility of polymer main chain would decrease by introducing rigid C=C double bonds. There was little difference among **P1a-e** on their BOD/TOD curves. It seemed to be difficult for *Z*-configuration C=C bond to clarify the substrate specificity of enzyme through those limited conformational variety.

End groups of such polyester samples were consisted of –COOH or –OH, that is, hydrophilicity was higher than the model compounds mentioned above. Generally speaking, hydrophilic compounds were preferred in hydrolysis by microorganism. The biodegradation of unsaturated polyesters **P1a-e** were differ from the case of the oligomeric model compounds (*Z*4 and *E*4) even though they have the approximately same molecu-

lar weight ($M_n = 1.0–1.1 \times 10^3$). The BOD/TOD value of **P2a** was 30.9% after 30 d, however, these values for **P2b-e** changed to much higher levels than that of **P2a**, as the proportion of *E*-configuration increased. This rate enhancement should be contributed by increasing of *E*-configuration fraction in the C=C double bonds. Now, it is obvious fact that *Z*- and *E*-configuration in the C=C double bonds affected their biodegradability in the different manner, especially in the polyesters having relatively high molecular weight. In other words, the biodegradation rate might be controlled by the introduction of some C=C double bond in chain of aliphatic polyester and furthermore adjusted finely depending on its *Z/E* ratio.

CONCLUSION

Unsaturated aliphatic polyesters **P1a** ($M_n = 1.3 \times 10^3$) and **P2a** ($M_n = 3.5 \times 10^3$) were prepared from

MAn and EG by the use of solution polycondensation method. In order to investigate geometrical effects as well as effects of molecular weight on biodegradability, polyesters **P1b-e** and **P2b-e** were derived from one original polymer **P1a** or **P2a**, respectively, by isomerization reaction from *Z*- to *E*-configuration in DCE by using Mor. There was little difference concerning the biodegradability of **P1a-e**, suggesting that oligomeric polyesters with the molecular weight around 1300 could be degraded by microorganism irrespective of their geometrical structures. However, an effect of the molar ratio of *Z*-/*E*-configuration at the C=C double bonds could be found on the biodegradability of **P2a-e** having much longer chain length than **P1a-e**. The biodegradability of *E*-configuration rich polyesters was clearly superior to *Z*-rich one with regard to biodegradability of **P2a-e**. When molecular weight (M_n) of oligomeric model compounds were more than *ca.* 1000, it can be recognized that the preferable biodegradability of *E*-configuration could come out clearly, even though the hydrophobicity of oligomeric model compounds influenced on their biodegradability in the different manner. Thus the effects of configuration of C=C double bonds could be estimated separately from the effects due to their chain length.

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