

Effects of Geometrical Difference of Unsaturated Aliphatic Polyesters on Their Biodegradability II. Isomerization of Poly(maleic anhydride-*co*-propylene oxide) in the Presence of Morpholine

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ABSTRACT: Ring-opening copolymerizations of succinic anhydride (SAn, **1**) or maleic anhydride (MAn, **2**) with propylene oxide (PO) were carried out by using magnesium diethoxide (Mg(OEt)₂) as a catalyst. The unsaturated polyester (**P2a**) was found to have only *Z*-configuration around a C=C double bond from its ¹H and ¹³C NMR spectra. Isomerization reaction of **P2a** from *Z*- to *E*-configuration was performed in 1,2-dichloroethane with a catalytic amount of morpholine. Thus unsaturated polyesters, **P2b-e**, having the same molecular weight but the different ratio of *Z*-/*E*-configuration could be optionally prepared from one original polymer **P2a** by controlling isomerization reaction time. Biodegradability of these polyester samples was evaluated from their biochemical oxygen demand (BOD) values in the presence of an activated sludge. Polyester **P2a** was hardly degraded during measurement. However, polyesters **P2b-e**, partially containing *E*-configuration of the C=C double bond, degraded considerably faster than **P2a** itself. The biodegradability of saturated polyester **P1** was also examined to compare with the **P2**-series.

KEY WORDS Biodegradability / Unsaturated Polyester / Geometrical Isomer / Ring-Opening Copolymerization / Cyclic Acid Anhydride / Propylene Oxide /

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 almost all of synthetic polymers are disposed after use, however, those cause serious environmental problems. Thus, biodegradable polymers have received much attention in recent years as one of the answer to solve the problems. In fact, biodegradable polymers, especially aliphatic polyesters, have been widely investigated by many scientists in the world.

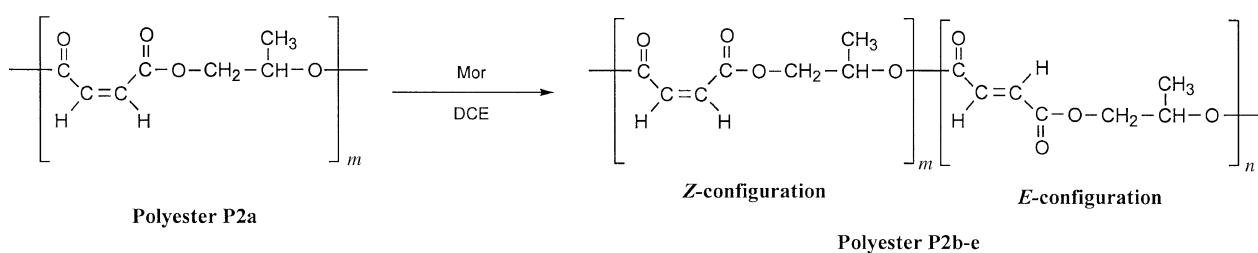
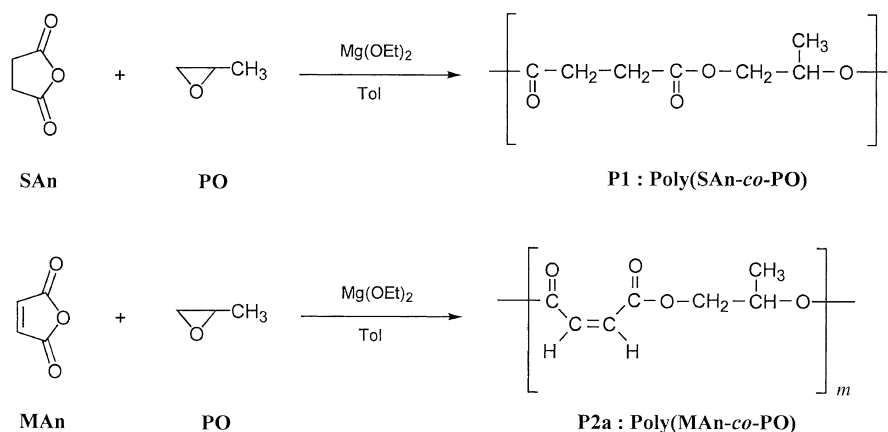
In spite of a large number of studies on biodegradability of polyesters, little attention has been given to unsaturated polyesters.^{1–6} Tokiwa and Suzuki reported that a few unsaturated polyesters containing 2-butenediol unit could be hydrolyzed by lipase.¹ On the other hand, slightly cross-linked 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. In controlling the biodegradation rate of polyester, it is very helpful to make geometrical effects clear. In our previous paper,⁶ 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 unsaturated polyesters but introducing *E*-configuration did not affect so remarkably. However, the variety of samples was limited because of the difficulty in preparation of samples having the same molecular weight and the different *Z*/*E* ratio. Although polycondensation method of unsaturated acid anhydrides with diol in the presence of acid as a catalyst was employed in previous work, the C=C double bond of *Z*-configuration took place isomerization into *E*-configuration as a side reaction during polycondensation.^{7–10} This is a reason not to obtain 100% *Z*-configuration isomer. Moreover longer polymerization time so as to achieve polymers with high molecular weight resulted in higher contents of *E*-configuration.

In this paper, we employ ring-opening polymerization between acid anhydrides and epoxydes with a catalyst but not protonic catalyst.^{5, 11–13} Thus polyesters **P1** and **P2a** could be obtained from succinic anhydride (SAn, **1**) or maleic anhydride (MAn, **2**) with propylene oxide (PO), respectively. In accordance with our expectation, the resulting polyester **P2a** was confirmed as the polymer with 100% *Z*-configuration. Furthermore unsaturated polyesters have various *Z*/*E* ratios could be readily prepared through isomerization of one original polymer **P2a** in 1,2-dichloroethane (DCE) in the pres-

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ence of morpholine (Mor) as a catalyst.¹⁴ Molecular weight of the polyesters obtained by this process were nearly same with the original polymer sample (**P2a**). By using these samples having same molecular weight, geometrical effects on the biodegradability of unsaturated polyesters were studied in details.

EXPERIMENTAL

Materials

Succinic anhydride (SAn), and maleic anhydride (MAn) were purchased from Nacalai Tesque, Inc. These anhydrides were purified by recrystallization from chloroform (CHCl₃). Propylene oxide (PO) and magnesium ethoxide (Mg(OEt)₂) were available from Wako Pure Chemical Industries, Ltd. Morpholine (Mor) was also purchased from Nacalai Tesque, Inc. PO, Mor, Toluene (Tol), CHCl₃, and 1,2-dichloroethane (DCE) were purified by distillation before use.

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 were measured in CDCl₃ at 27°C by using a Bruker DPX-200 MHz spectrometer. The chemical shifts were expressed as δ value apart from tetramethylsilane (TMS). The number-average molecular weight (M_n) and poly-

dispersity index (M_w/M_n) of polymers were determined by gel permeation chromatography (GPC) method, calibrated with polystyrene standards. A GPC system of Tosoh HLC-8020 equipped with a Tosoh RI-8020 detector and Tosoh G2000-HXL, G3000-HXL, G4000-HXL, and G5000-HXL columns was run at 40°C. 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 220C in a range from -100 to 120°C at a heating rate of 10°C min⁻¹.

Synthesis of Poly(succinic anhydride-co-propylene oxide) (**P1**)

A mixture of 0.83 g (14.3 mmol) of PO and 1.40 g (14.3 mmol) of SAn was dissolved in 2.0 mL of Tol in a glass tube at room temperature under the nitrogen atmosphere. This mixture was then polymerized by adding 0.013 g (0.11 mmol) of Mg(OEt)₂. After stirring at 100°C for 48 h, the mixture was diluted with CHCl₃ and then washed with water containing a trace amount of HCl to remove inorganic components completely. The organic solution was poured into diethyl ether, and the supernatant was removed by decantation. After reprecipitation from CHCl₃ solution into diethyl ether (as a non-solvent), the polymeric materials were collected and dried *in vacuo* to give polyester **P1** [Yield; 0.88 g, 39.1%, (**P1** in Table I)]. IR (KBr disk, cm⁻¹): 2984 [ν_{C-H}], 1736

Table I. Ring-opening copolymerization of SAn or MAn with PO using Mg(OEt)₂

Polyester	Monomer mmol		Mg(OEt) ₂ mmol	Toluene mL	Temp °C	Time h	Yield g (%)	M _n ^a ×10 ⁻³	M _w /M _n ^a	m ₁ /m ₂ ^b	Z/E ^c
P1	SAn (14.3)	PO (14.3)	0.114	2.0	100	48	0.88 (39.1)	5.0	1.34	50/50	–
P2a	MAn (142.8)	PO (142.8)	1.170	20.0	80	48	9.43 (42.2)	4.2	1.17	49/51	100/0

^aDetermined by GPC calculated by polystyrene standards; eluent, THF. ^bMolar ratio of MAn or SAn (*m*₁) unit to PO (*m*₂) unit in polymer, determined by ¹H NMR. ^cMolar ratio of *Z*- and *E*-conformation unit in polymer, determined by ¹H NMR.

Table II. *Z*- to *E*-configuration isomerization reaction of poly(MAn-*co*-PO) (**P2a**) in DCE in the presence of Mor^a

Polymer	Reaction Time min	Yield g (%)	Z/E ^b	M _n ^c ×10 ⁻³	M _w /M _n ^c	T _g ^d °C
P2a	–	–	100/0	4.2	1.17	–14.4
P2b	10	0.644 (82.6)	66/34	4.5	1.17	–7.0
P2c	30	0.637 (81.7)	37/63	4.8	1.15	–0.6
P2d	60	0.616 (79.0)	16/84	4.9	1.15	1.7
P2e	120	0.622 (79.7)	8/92	5.0	1.15	4.0

^aPolyester **P2a** = 0.780 g (5.0 mmol); Mor = 0.04 g (0.5 mmol); DCE = 10.0 mL; reaction temperature = 80°C. ^bMolar ratio of *Z*- and *E*-conformation unit in polymer, determined by ¹H NMR. ^cDetermined by GPC calculated by polystyrene standards; eluent, THF.

^dDetermined by DSC; heating rate, 10°C min⁻¹.

[ν_{C=O} (ester)], and 1156 [ν_{C–O–C} (ester)]. ¹H NMR (CDCl₃, δ ppm): 5.30–5.02 [OCH₂CH(CH₃)O], 4.29–3.98 [OCH₂CH(CH₃)O], 2.65–2.62 [OCH₂CH₂O], and 1.31–1.27 [OCH₂CH(CH₃)O]. ¹³C NMR (CDCl₃, δ ppm): 172.4 [CO], 68.9 [OCH₂CH(CH₃)O], 66.6 [OCH₂CH(CH₃)O], 29.5 [OCCH₂CH₂CO], and 16.8 [OCH₂CH(CH₃)O].

Synthesis of Poly(maleic anhydride-*co*-propylene oxide) (**P2a**)

Polyester **P2a** was prepared by a similar manner to that of polyester **P1**, except for the reaction temperature (80°C) [Yield; 9.43 g, 42.2% (**P2a** in Table I)]. IR (KBr disk, cm⁻¹): 2987 [ν_{C–H}], 1735 [ν_{C=O} (ester)], and 1161 [ν_{C–O–C} (ester)]. ¹H NMR (CDCl₃, δ ppm): 6.29–6.20 [CH=CH(*Z*-configuration)], 5.35–5.16 [OCH₂CH(CH₃)O], 4.31–4.23 [OCH₂CH(CH₃)O], and 1.34–1.30 [OCH₂CH(CH₃)O]. ¹³C NMR (CDCl₃, δ ppm): 164.7 [CO], 130.5–129.3 [CH=CH (*Z*-configuration)], 69.2 [OCH₂CH(CH₃)O], 66.4 [OCH₂CH(CH₃)O], and 16.2 [OCH₂CH(CH₃)O].

Isomerization Reaction of Polyester (**P2a**)

A typical experimental procedure is as follows. Polyester **P2a** (0.78 g, 5.0 mmol) was placed into a 50 mL round-bottomed flask equipped with reflux condenser, dissolved completely in 10.0 mL of DCE at room temperature under the nitrogen atmosphere. After Mor (0.04 g, 0.5 mmol) had been added, the flask was immediately immersed in an oil bath and heated up to 80°C. The mixture was stirred by magnetic stirrer at 80°C for 10–120 minutes. After cooling down to room temperature, the mixture was diluted with CHCl₃, and then the organic layer was poured

into diethyl ether to obtain precipitate. The precipitate was collected and dried *in vacuo* at room temperature to give polyester **P2b–e** [Yield; 0.644 g, 82.6%, for polyester **P2b**, the others are in Table II]. IR (KBr disk, cm⁻¹): 2986 [ν_{C–H}], 1726 [ν_{C=O} (ester)], and 1158 [ν_{C–O–C} (ester)]. ¹H NMR (CDCl₃, δ ppm): 6.91–6.81 [CH=CH(*E*-configuration)], 6.30–6.20 [CH=CH(*Z*-configuration)], 5.37–5.16 [OCH₂CH(CH₃)O], 4.38–4.14 [OCH₂CH(CH₃)O], and 1.36–1.31 [OCH₂CH(CH₃)O]. ¹³C NMR (CDCl₃, δ ppm): 165.0 [CO], 134.0–133.7 [CH=CH (*E*-configuration)], 130.9–129.7 [CH=CH (*Z*-configuration)], 69.5 [OCH₂CH(CH₃)O], 66.8 [OCH₂CH(CH₃)O], and 16.8 [OCH₂CH(CH₃)O].

Biochemical Oxygen Demand (BOD) Test

Biochemical oxygen demand (BOD) value of the samples was determined by the oxygen consumption method according to the JIS K 6950 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 K₂HPO₄ (217.5), KH₂PO₄ (85.0), Na₂HPO₄·2H₂O (334.0), NH₄Cl (5.0), CaCl₂·2H₂O (36.4), MgSO₄·7H₂O (22.5), FeCl₃·6H₂O (0.25 mg L⁻¹), kept at pH = 7.4 ± 0.1. Since polyester **P1**, and **P2a–e** were viscous liquid, each sample in chloroform solution was cast to film on bottom of the bottle in height of 2 cm. The concentration of polymers in the incubation medium was 100 mg L⁻¹.

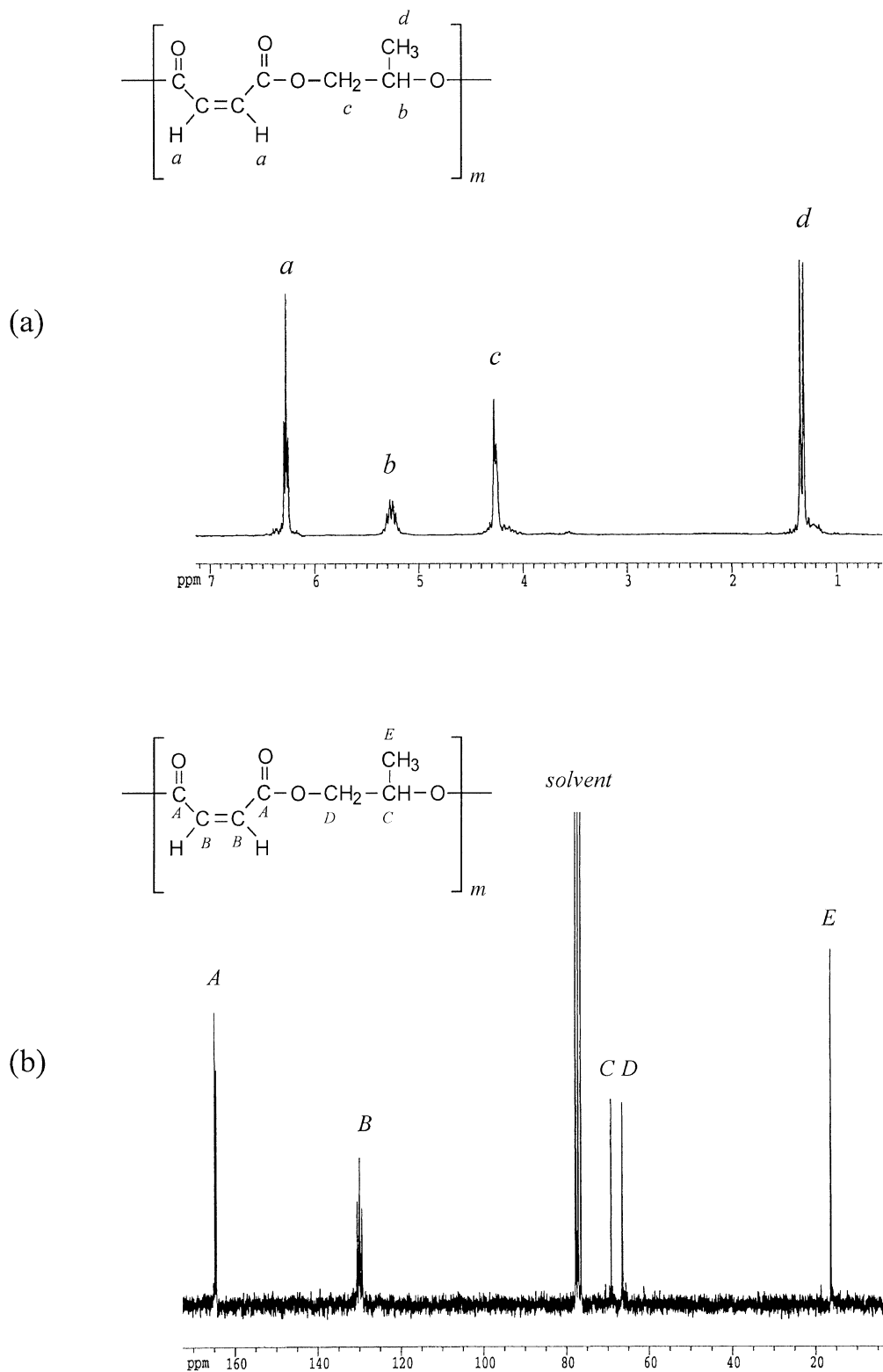


Figure 1. NMR spectra of poly(MAn-*co*-PO) (**P2a**, in Table I) in CDCl₃ at 27°C; (a) ¹H NMR, (b) ¹³C NMR.

RESULTS AND DISCUSSION

Ring-Opening Copolymerization of Acid Anhydrides and Propylene Oxide

In our previous study, poly(maleic anhydride-*co*-ethylene glycol) were synthesized by solution polycon-

densation method.⁶ *Z*-conformation rich unsaturated polyester (molar ratio *Z/E* = 81/19) could be prepared, but 100% *Z*-conformation was never obtained because of the C=C double bond of *Z*-configuration isomerized into *E*-configuration as a side reaction during polycondensation. To clarify geometric structure effects on their biodegradability, ring-opening copolymerization

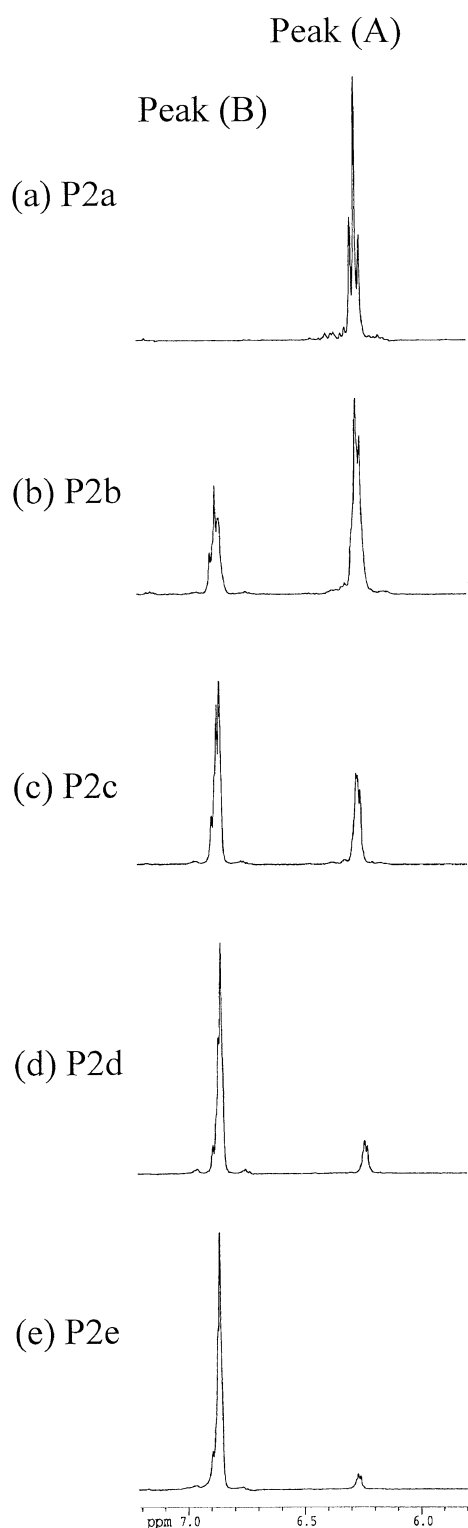


Figure 2. ^1H NMR spectra along reaction time for the isomerization of polymer **P2a**.

of SAn or MAn with PO were examined according to Scheme 1.^{5, 11–13} The results are summarized in Table I.

In the synthesis of polyester **P1** and **P2a**, light-brown viscous samples having no T_m could be obtained. The NMR spectra for polyester **P2a** are shown in Figure 1. Although small peaks around 6.3, 4.1, and 1.2 ppm could be assigned

to terminal $-\text{COCH}=\text{CHCOOH}$ (*Z*-configuration), $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$, and $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$ respectively, very few peaks around 3.6 ppm assignable to homosequence of PO could be observed in the NMR spectra. The molar ratios of SAn or MAn unit to PO unit in the polymers, m_1/m_2 , were almost 50/50 within experimental error. The geometrical structure of C=C double bonds in polyester **P2a** was confirmed as only *Z*-configuration by ^1H and ^{13}C NMR analyses.

The polymer **P1** and **P2a** obtained by ring-opening copolymerization method were essentially linear polymers soluble in CHCl_3 completely, but molecular weight (M_n) over 10^4 could not be achieved as well as solution polycondensation method described in our previous work.⁶ In the case of saturated polyesters, chain extension reaction is often employed to make up polyester having high molecular weight.^{15, 16} In order to obtain high molecular weight of unsaturated polyester samples, chain extension reaction of polymer **P2a** was also examined by using a Titanium(IV) isopropoxide as a catalyst at 80°C . However it resulted in gelation of the polymer in parallel with the chain extension reaction. In our experimental knowledge, the unsaturated polyesters were tended to face with cross-linking when their molecular weight became over about 5000. Therefore it seems that preparation of linear unsaturated polyesters having high molecular weight is difficult.

Taking a few reports into consideration, strange behavior of a few samples for biodegradation test in the previous works might be subject to effects of cross-linking even if it occurred slightly.^{1, 3, 4} To estimate distinct geometrical effects in biodegradation test, the sample should be required to avoid cross-linking and, as a result, have rather moderate degree of polymerization. The present samples are suitable for the above requirement.

Isomerization of Polymer P2a Catalyzed by Mor

It is one of the final goal for us to design various types of chemical system for controlling the biodegradation rate of polymers. For this purpose, our attention has been focused upon how much degree the different *Z/E* ratios of C=C double bonds in the unsaturated aliphatic polyesters affect their biodegradability. Therefore it is worth while preparing some unsaturated polyesters having a wide variety of the *Z/E* ratio.

One reasonable route could be established in this work. It is well known the C=C double bond in *Z*-configuration can be isomerized into *E*-configuration in the presence of some amine compounds as a catalyst.¹⁴ Thus isomerization of polyester **P2a** having all *Z*-configuration of C=C double bonds was examined with

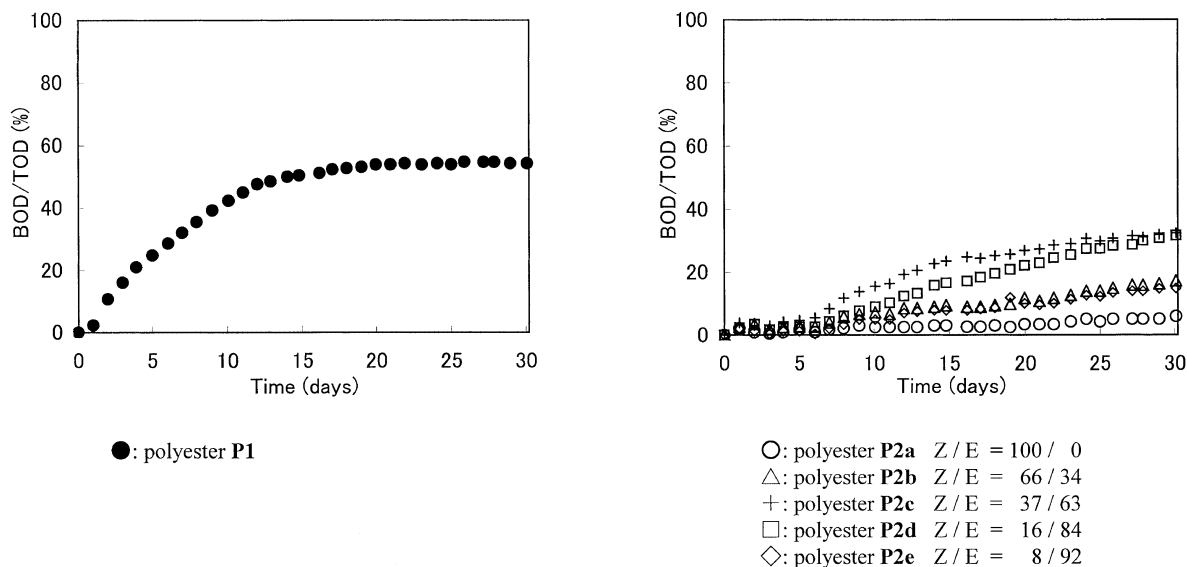


Figure 3. Biodegradability of saturated polyester **P1** and unsaturated polyester **P2a-e** evaluated by biochemical oxygen demand (BOD).

Mor. The results are summarized in Table II, showing that an optional *Z/E* ratio in the unsaturated polyesters can be achieved without any serious troubles.

Figure 2 represents ^1H NMR spectra of a series of polyester **P2a-e** derived through isomerization of polymer **P2a**. The occurrence of isomerization from *Z*- to *E*-configuration was clearly confirmed by the appearance of peak (B) at about 6.8 ppm which could be assigned to olefinic methine proton of *E*-configuration. As reaction time was prolonged longer, the intensity of peak (B) became stronger. Instead, the intensity of peak (A) at about 6.2 ppm assignable to methine protons of *Z*-configuration was decreased gradually. The molar fraction ratios of *Z*-/*E*-configuration of $-\text{C}=\text{C}-$ moiety in the samples could be calculated from the intensity ratios of peak (A)/peak (B). These numerical data are summarized in Table II. Thus unsaturated polyesters, **P2b-e**, having the same molecular weight but the different ratio of *Z*-/*E*-configuration could be optionally prepared from one original polymer **P2a** by controlling isomerization reaction time. The variety of *Z/E* values was wide enough to investigate geometrical effects on biodegradability.

The molar ratio of maleic and fumaric acid unit to PO unit in polyester **P2a-e** [$m_1/m_2 = (m_{\text{MA}_n} + m_{\text{FA}})/m_{\text{PO}}$] was, of course, kept as 50/50. Furthermore, each molecular weight (M_n) of polyesters containing the original **P2a** was found to be similar irrespective of the different *Z/E* value. This is a very important advantage because there is no need to discuss the effects of molecular weight of the samples on their biodegradability.

Glass transition temperature (T_g) of the above polyesters was determined by DSC. As the fraction of *E*-configuration went on increasing, T_g raised up grad-

ually. Therefore it is presumed that increase of the fraction of *E*-configuration might bring their structure to certain regularity (crystalline character) even though T_m were not observed clearly as yet.

Biochemical Oxygen Demand Test

Biochemical oxygen demand (BOD) values of the above mentioned samples in the presence of an activated sludge were measured by a BOD tester for 30 days. The relationship of BOD/TOD values vs. elapse of time can be plotted as Figure 3.

The BOD/TOD values of saturated polyester **P1** were 54.3% after 30 days, however, these values of unsaturated polyesters **P2a-e** were region of 5.9 (**P2a**) to 32.4% (**P2c**) after 30 days. Introducing of $\text{C}=\text{C}$ double bonds to aliphatic polyester made more or less the rate of the degradation slow down. Especially polyester **P2a** having all *Z*-configuration of $\text{C}=\text{C}$ double bonds was found to degrade hardly in the course of the BOD test. However polyester **P2b** (*E*-configuration fraction: 34%) and **P2c** (*E*-configuration fraction: 63%) became to degrade much faster than polyester **P2a**. This rate enhancement should be contributed by increasing of *E*-configuration fraction in the $\text{C}=\text{C}$ double bonds. It is now obvious fact that *Z*- and *E*-configuration in the $\text{C}=\text{C}$ double bonds affected their biodegradability in the different manner, suggesting that the difference in geometrical structure might be recognized by microorganisms in an activated sludge. In other words, the biodegradation rate can be controlled by the introduction of some $\text{C}=\text{C}$ double bond in chain of aliphatic polyester and further adjusted finely depending on its *Z/E* ratio.

When the *E*-configuration fraction increased over

84%, however, degradation rate of the samples was suppressed against our expectation. There are many articles in which the effect of crystallinity of the sample on its biodegradability was pointed out.^{17, 18} Generally speaking, highly crystalline polyester samples tend to inhibit their smooth degradation by microorganisms, regardless of its chemical structure. It was already noted that rising-up of T_g was observed as increasing of the *E*-configuration fraction (Table I). Therefore this reversion in *E*-configuration rich region suggests that the biodegradability of these samples must be controlled by not only preference due to the geometrical structure but also other factors, maybe its crystallinity etc.

CONCLUSION

Unsaturated and saturated aliphatic polyesters (**P2a** and **P1**) were synthesized by ring-opening copolymerization of corresponding anhydrides with PO. The geometrical structure of C=C double bonds in polyester **P2a** was found to be 100% *Z*-configuration, in contrast with the solution polycondensation of unsaturated acid anhydrides with ethylene glycol using a protonic catalyst. In order to investigate geometrical effects on biodegradability, polyesters **P2b-e** were derived from one original polymer **P2a** by isomerization reaction from *Z*- to *E*-configuration in DCE in the presence of Mor. It is clear that the different geometrical structure of the polymer, *Z*- and *E*-configuration in the C=C double bonds, affected to their biodegradability. Especially polyester **P2a** having all *Z*-configuration of C=C double bonds was found to degrade hardly in the course of the BOD test. The biodegradability of *E*-configuration was found to be superior to *Z*-configuration. In order to discuss biodegradation rate of polyesters strictly,

it might be necessary to take into account their crystallinity, too.

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