Effects of Geometric Structure in Unsaturated Aliphatic Polyesters on Their Biodegradability

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ABSTRACT: Melt or solution polycondensation of cyclic anhydrides (succinic, methylsuccinic, maleic, and citraconic) or fumaric acid with ethylene glycol was conducted under various conditions. The resulting unsaturated polyesters were found to have various ratios of different two configurations at the C=C double bond from their ^{1}H and ^{13}C NMR spectra. The biodegradability of these polyester samples was evaluated from enzymatic degradation tests with *Rizopous delemar* lipase, and biochemical oxygen demand (BOD) values in an activated sludge. Introducing methyl group on the polymer chain tends to reduce its biodegradability. In comparison with saturated polyesters, efficient biodegradation was prevented by unsaturated monomer units, particularly by *Z*-configuration of C=C double bond.
    KEY WORDS   Biodegradability / Unsaturated Polyester / Geometrical Isomerization / Polycondensation / Cyclic Anhydride /

Synthetic polymeric materials have provided many advantages in our daily life for the last century, and become one of the most important materials. However, when once polymer substances are disposed after use they cause serious environmental problems. Thus, biodegradable polymers have received much attention in recent years to solve this problem. In fact, biodegradable polymers, especially aliphatic polyesters, have been widely investigated by many scientists.

Itaconic acid is one of the elements of some fungi (*Aspergillus terreus*, *A. itaconicus*, etc.). Commercially, itaconic acid is produced by the cultivation of *Aspergillus terreus* with molasses or glucose.[1] Thus, itaconic acid will be an excellent candidate for design of biodegradable polymeric materials. We have examined to design biodegradable polyesters using itaconic acid and its derivatives.[2] Itaconic acid involves a >C=CH$_2$ type of double bond in its chemical structure, which tend to isomerize readily into =C(CH$_3$)– group in the course of polymerization. Therefore, we attempt to clarify effects of such unsaturated bond or methyl group in aliphatic polyester chain on their biodegradability.

Tokiwa and Suzuki reported that unsaturated polyesters containing 2-butenediol unit could be hydrolyzed by lipase, but slightly cross-linking unsaturated polyesters, poly(hexamethylene fumarate) and poly(*cis*-2-butene fumarate), were hardly hydrolyzed by lipase.[3] Recently, further studies on unsaturated polyesters were reported by other research groups.[4—7]

However, only few investigations have been reported on biodegradability of unsaturated polyesters.

A carbon–carbon double bond in unsaturated polyesters has two geometrical isomers (*Z*- and *E*-configuration), and it should affect biodegradability. In order to control the rate of biodegradation of polyesters, it is important to clarify geometrical effect on biodegradation.

In this paper, we aimed to prepare the polyesters containing C=C double bond or methyl side chain. Saturated polyesters (**1** and **2**) and unsaturated ones (**3** and **4**) were synthesized by polycondensation of the corresponding anhydrides or fumaric acid with ethylene glycol, respectively. The resulting unsaturated polyesters were found to have a various ratios of different *Z*-/*E*-configuration at the C=C double bond. The biodegradability of polyesters obtained was evaluated from enzymatic degradation tests and biochemical oxygen demand (BOD) values in an activated sludge.

EXPERIMENTAL

Materials

Succinic anhydride (SAn), maleic anhydride (MAn), fumaric acid (FA), ethylene glycol (EG), and *p*-toluenesulfonic acid (*p*-TsOH) were purchased from Nacalai Tesque, Inc., Kyoto, Japan. These anhydrides were purified by recrystallization from chloroform. Methylsuccinic anhydride (MSAn) was purchased from Aldrich Chem. Co. Citraconic anhydride (CAn) was kindly provided from Iwata Chemical Co.,

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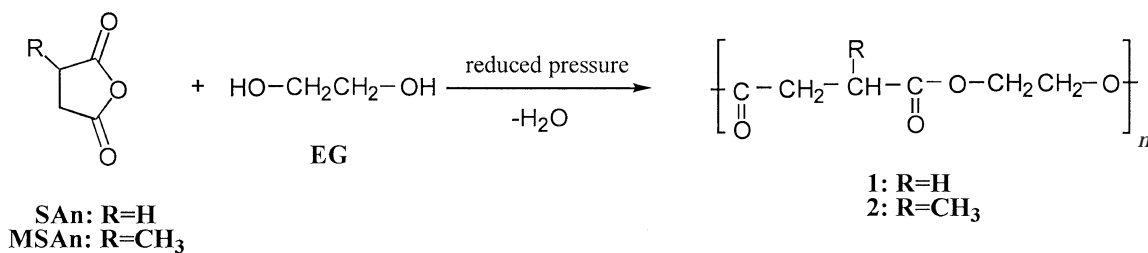
Scheme 1. Melt polycondensation of saturated cyclic anhydrides with EG.
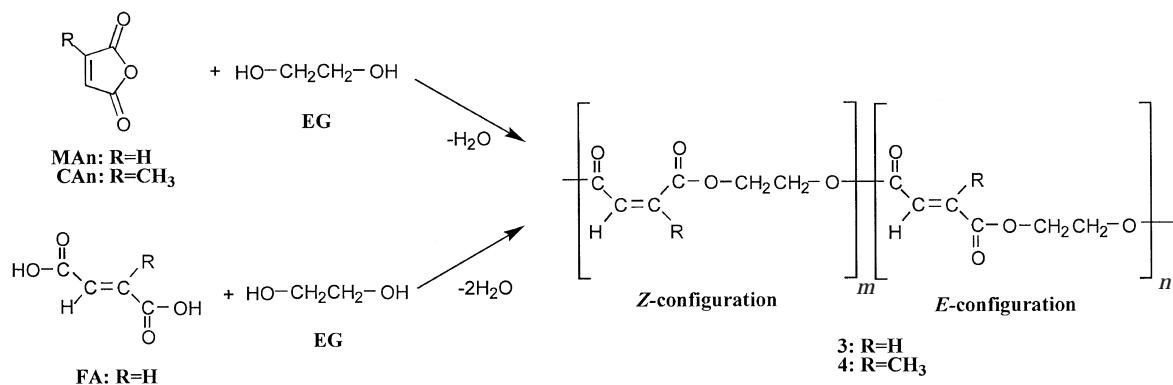
Scheme 2. Solution polycondensation of unsaturated cyclic anhydrides or FA with EG.

Ltd. (Shizuoka, Japan). MSAn and CAn purified by distillation under reduced pressure before use. Toluene (Tol) and *o*-dichlorobenzene (*o*-DCB) were also purified by distillation immediately before use. Dimethyl succinate and methylsuccinate were purchased from Aldrich Chem. Co. Dimethyl maleate and fumarate were also purchased from Tokyo Kasei Kogyo Co., LTD.

Measurement

FT-IR spectra were recorded for film samples cast on KBr disk from chloroform solutions, using a JASCO FT/IR-430 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ at 27°C using a Bruker DPX-200 MHz spectrometer (200 MHz). 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. In most cases, tetrahydrofuran was used as an eluent. Thermal properties including glass transition temperature (T_g) and melting point (T_m) 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}.

Melt Polycondensation

Synthesis of Poly(SAn-co-EG) (1). SAn (2.58 g, 25.8 mmol) and EG (1.66 g, 26.8 mmol) were placed into a 50 mL round-bottomed flask equipped with a magnetic stirrer, and a nitrogen gas inlet. The flask was immersed in an oil bath and heated up to 180°C gradually. Water produced during reaction and excess EG were removed under a reduced pressure (0.5 mmHg). The reaction mixture stood at 180°C under a reduced pressure for 24–48 h. After cooling, the mixture was diluted with chloroform, and then the organic solution was poured into diethyl ether to obtain white precipitate. The precipitate was collected and dried *in vacuo* at room temperature to give white solid polyester **1** [Yield; 2.94 g, 79.0%, (run 1 in Table I)]. IR (KBr disk, cm^{-1}): 2967 (ν_{C-H}), 1732 [$\nu_{C=O}$ (ester)], and 1161 [ν_{C-O-C} (ester)]. ^{1}H NMR (CDCl$_3$, δ ppm): 4.30 (OC*H*$_2$C*H*$_2$O), and 2.67 (COC*H*$_2$C*H*$_2$CO). ^{13}C NMR (CDCl$_3$, δ ppm): 172.3 (*C*O), 62.4 (O*C*H$_2$*C*H$_2$O), and 29.0 (OC*C*H$_2$*C*H$_2$CO).

Synthesis of Poly(MSAn-co-EG) (2). Polyester **2** was prepared by a similar manner to that of polyester **1** [Yield; 94.7% (run 4 in Table I)]. IR (KBr disk, cm^{-1}): 2976 (ν_{C-H}), 1735 [$\nu_{C=O}$ (ester)], and 1161 [ν_{C-O-C} (ester)]. ^{1}H NMR (CDCl$_3$, δ ppm): 4.29 (OC*H*$_2$C*H*$_2$O), 3.49–2.86 (CH$_3$C*H*CO), 2.83–2.71 and 2.47–2.39 (COC*H*$_2$), and 1.25–1.22 (C*H*$_3$CHCO). ^{13}C NMR (CDCl$_3$, δ ppm): 174.9 (CH$_3$*C*HCO), 171.9 (*C*OCH$_2$), 62.3 (O*C*H$_2$*C*H$_2$O), 37.2 (*C*OCH$_2$), 35.6 (CH$_3$*C*HCO), and 16.9 (*C*H$_3$CHCO).

Solution Polycondensation

Synthesis of Poly(MAn-co-EG) (3a). Unsaturated type polyesters were prepared by a conventional solution polycondensation. 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 *p*-TsOH as a catalyst were placed into a 100 mL round-bottomed flask equipped with a magnetic stirrer, 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. The resulting polyester was pulified by the same manner as those of polyester **1** and **2** [Yield; 11.6 g, 81.6% (run 6 in Table II)]. IR (KBr disk, cm^{-1}): 2961 (ν_{C-H}), 1729 [$\nu_{C=O}$ (ester)], 1646 ($\nu_{C=C}$), 1159 [ν_{C-O-C} (ester)]. ^{1}H NMR (CDCl$_3$, δ ppm): 6.91 [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 (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).

Synthesis of Poly(MAn-co-EG) (3b). MAn (9.81 g, 100.0 mmol), EG (6.21 g, 100.0 mmol), *o*-DCB, and *p*-TsOH as a catalyst were placed into a 100 mL round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap with a reflux condenser, and a nitrogen gas inlet. The reaction mixture was refluxed at 160°C for 12 h under a stream of nitrogen. Purification of polyesters was the same as described above [Yield; 10.9 g, 76.8% (run 7 in Table II)]. IR (KBr disk, cm^{-1}): 2961 (ν_{C-H}), 1727 [$\nu_{C=O}$ (ester)], 1646 ($\nu_{C=C}$), and 1157 [ν_{C-O-C} (ester)]. ^{1}H NMR (CDCl$_3$, δ ppm): 6.91 [C*H*=C*H* (*E*-configuration)], 6.31 [C*H*=C*H* (*Z*-configuration)], and 4.43 (OC*H$_2$*C*H$_2$*O). ^{13}C NMR (CDCl$_3$, δ ppm): 164.8 (*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).

Synthesis of Poly(FA-co-EG) (3c). The preparation method was similar to that of *poly(MAn-co-EG)* (**3a**), except for the use of FA (9.81 g, 100.0 mmol) instead of MAn. Although a little portion of FA was not dissolved in toluene, polycondensation reaction was continued as it was under the given conditions [Yield; 8.71 g, 61.2% (run 8 in Table II)]. IR (KBr disk, cm^{-1}): 2960 (ν_{C-H}), 1719 [$\nu_{C=O}$ (ester)], 1646 ($\nu_{C=C}$), and 1156 [ν_{C-O-C} (ester)]. ^{1}H NMR (CDCl$_3$, δ ppm): 6.91 [C*H*=C*H* (*E*-configuration)], and 4.47 (OC*H$_2$*C*H$_2$*O). ^{13}C NMR (CDCl$_3$, δ ppm): 164.5 (*C*O), 133.6 [*C*H=*C*H (*E*-configuration)], and 62.8 (O*C*H$_2$*C*H$_2$O).

Synthesis of Poly(CAn-co-EG) (4a). The preparation method was similar to that of **3a**, except for the use of CAn (11.2 g, 100.0 mmol) instead of MAn [Yield; 10.32 g, 65.9% (run 9 in Table II)]. IR (KBr disk, cm^{-1}): 2959 (ν_{C-H}), 1735 [$\nu_{C=O}$ (ester)], 1653

($\nu_{C=C}$), and 1169 [ν_{C-O-C} (ester)]. ^{1}H NMR (CDCl$_3$, δ ppm): 6.81 [COC*H*=CCH$_3$CO (*E*-configuration)], 6.36 and 5.77 (C*H$_2$*=C due to itaconic acid unit), 5.89 [COC*H*=CCH$_3$CO (*Z*-configuration)], 4.58–4.23 (OC*H$_2$*C*H$_2$*O), 3.37 [COC*H$_2$* (due to itaconic acid unit), 2.29 [COCH=CC*H$_3$*CO (*E*-configuration)], and 2.07 [COCH=CC*H$_3$*CO (*Z*-configuration)]. ^{13}C NMR (CDCl$_3$, δ ppm): 168.5 [COCH=CCH$_3$*C*O (*E*-configuration)], 166.7 [COCH=CCH$_3$*C*O (*Z*-configuration)], 165.4 [*C*OCH=CCH$_3$CO (*E*-configuration)], 164.4 [*C*OCH=CCH$_3$CO (*Z*-configuration)], 146.2 [COCH=*C*CH$_3$CO (*Z*-configuration)], 144.1 [COCH=*C*CH$_3$CO (*E*-configuration)], 126.6 [CO*C*H=CCH$_3$CO (*E*-configuration)], 120.4 [CO*C*H=CCH$_3$CO (*Z*-configuration)], 62.8–62.2 (O*C*H$_2$*C*H$_2$O), 20.5 [COCH=C*C*H$_3$CO (*Z*-configuration)], and 14.4 [COCH=C*C*H$_3$CO (*E*-configuration)].

Enzymatic Degradation Test

Enzymatic degradation test was carried out as follows. Since polyester **2**, **3a**, and **3b** were viscous liquid, each 20 mg in chloroform solution was casted to form sample film on bottom of the test tube at 1 cm height. 2.0 mL of phosphate buffer (KH$_2$PO$_4$/K$_2$HPO$_4$, pH 5.6) and 100 units of *Rizopous delemar* lipase (Seikagaku Co.) were added in a test tube. A blank test was conducted for the polymer in the same phosphate buffer without the enzyme. The enzymatic tests were carried out for 12–96 h. After incubation, 6.0 mL of distilled water was added to the crude and the solution was subjected to centrifugation, then the supernatant solution was decanted. This washing process was repeated three times to the complete removal of enzyme. At last the recovered sample was dried to the constant weight under the reduced pressure.

Biochemical Oxygen Demand (BOD) Test

Biochemical oxygen demand (BOD) value was determined using a BOD tester (Model 200F, TAITEC Co., Koshigaya, Japan) by the oxygen consumption method and basically according to the JIS K 6950 at 25°C using an activated sludge from municipal disposal plant in Nagoya. The incubation medium was follows (mg L^{-1}): K$_2$HPO$_4$, 217.5; KH$_2$PO$_4$, 85.0; Na$_2$HPO$_4$ · 2 H$_2$O, 334.0; NH$_4$Cl, 5.0; CaCl$_2$ · 2 H$_2$O, 36.4; MgSO$_4$ · 7 H$_2$O, 22.5; FeCl$_3$ · 6 H$_2$O, 0.25 (pH = 7.4). The sample film was casted on bottom of the bottle within the prescribed height from chloroform solutions. The concentration of polymers in the incubation medium was 100 mg L^{-1}.

Table I. Melt polycondensation of SAn or MSAn with EG

Run	Polymer type	Monomer mmol	Temp °C	Time h	Yield %	$M_n{}^a$ ×10^{-3}	$M_w/M_n{}^a$	$T_g{}^b$ °C	$T_m{}^b$ °C
1	1	SAn(25.8) EG(26.8)	180	24	79.0	4.5	1.8	−19.8	100.4
2	1	SAn(25.8) EG(26.8)	180	36	81.9	8.2	1.8	−17.7	102.4
3	1	SAn(25.8) EG(26.8)	180	48	70.8	20.5	1.8	−22.1	97.7
4	2	MSAn(22.5) EG(23.2)	180	24	94.7	4.3	1.7	−36.6	–^{c}
5	2	MSAn(22.5) EG(23.2)	180	48	92.7	8.5	1.8	−26.2	–^{c}

[a]Determined by GPC calculated by polystyrene standards; eluent, CHCl$_3$ (run 1–3) or THF (run 4,5). [b]Determined by DSC; heating rate, 10°C min^{-1}. [c]Not detected.

Table II. Solution polycondensation of unsaturated cyclic anhydrides or FA with EG[a]

Run	Polymer type	Monomer mmol	Solvent[b] mL	Temp °C	Time h	Yield %	$M_n{}^c$ ×10^{-3}	$M_w/M_n{}^c$	$T_g{}^d$ °C	$T_m{}^d$ °C	Z/E[f]
6	3a	MAn (100.0) EG (100.0)	Tol(50.0)	130	24	81.6	2.9	1.8	−19.1	–^{e}	81/19
7	3b	MAn (100.0) EG (100.0)	o-DCB(50.0)	160	12	76.8	3.4	1.9	−25.5	–^{e}	60/40
8	3c	FA (100.0) EG (100.0)	Tol(50.0)	130	24	61.2	2.9	1.9	−30.2	64.9	0/100
9	4a	CAn (100.0) EG (100.0)	Tol(10.0)	130	24	65.9	3.8	1.4			88/12

[a]$[p\text{-TsOH}]_0 = 1.0$ mol%. [b]Tol = Toluene; o-DCB = o-dichlorobenzene. [c]Determined by GPC calculated by polystyrene standards; eluent, THE. [d]Determined by DSC; heating rate, 10°C min^{-1}. [e]Not detected. [f]Molar ratio of Z- and E-configuration unit in polymer, determined by ^{1}H NMR.

RESULTS AND DISCUSSION

Melt Polymerization

According to Scheme 1, melt polycondensation of saturated anhydrides with EG was examined under various reaction conditions (Table I).

In the synthesis of poly(SAn-co-EG) (**1**, run 1–3 in Table I), white powder samples could be obtained at room temperature with their molecular weight (M_n) from 4.5×10^3 to 20.5×10^3 which depended on a reaction time. On the other hand, light-brown viscous sample having no T_m was obtained in the synthesis of poly(MSAn-co-EG) (**2**, run 4, and 5). Molecular weight of polyester **2** reached to 8.5×10^3 through the polymerization for 48 h at 180°C.

Solution Polycondensation

Polyesters containing an unsaturated unit, however, could not be recovered well through a melt polycondansation method because of gelation at the initial stage. Therefore solution polycondensation shown in Scheme 2 was applied to the synthesis of unsaturated polyester **3** and **4**.[8–11] It is well known that the C=C double bonds of Z-configuration often isomerize into E-configuration during reaction of unsaturated anhydrides with diols in the presence of an acid catalyst.[12–15] It should be important for us to design various types of polymers for controlling biodegradation rate. We here focused on clarifying how configuration ratios of the unsaturated polyesters affect their biodegradability. Therefore the preparation of polyester samples hav-

ing a wide variety in the fraction of different two configurations was also examined in detail in this work. The result is summarized in Table II.

Figure 1 shows ^{1}H NMR spectrum of the poly(MAn-co-EG) (**3a**, run 6 in Table II). The occurrence of isomerizing at the C=C double bond was confirmed by the appearance of two peaks at 6.91 and 6.31 ppm in ^{1}H NMR, and at 133.6 and 129.9 ppm in ^{13}C NMR spectrum. These peaks could be assigned to methine protons and carbons of E- and Z-configuration, respectively. The molar ratio of Z-/E-configuration in the samples could be determined by the intensity ratio of peak b/a shown in Figure 1. When reaction temperature was raised up to 160°C, the isomerization was accelerated (**3b**, run 7). Using FA instead of MAn monomer resulted in giving the polyester with 100% E-configuration (**3c**, run 8).

In ^{1}H NMR spectra, broad peaks at 3.6–3.9 ppm were observed. These should be assignable to methylene protons [–CH$_2$CH$_2$OCH$_2$CH$_2$O–] in EG–EG linkage. Since EG is known to 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. In fact, these peaks due to EG–EG linkage became larger, as the composition ratio of two monomer units deviated more remarkably from 1:1. However, almost all samples used in our experiments were consisted of nearly 1:1 composition and the content of ether units could be recognized as rather low (less than about 6%). In other words to say, the sample should be composed of 47 ester and 3 ether units even in the maximum content of ether linkage. Biodegrad-
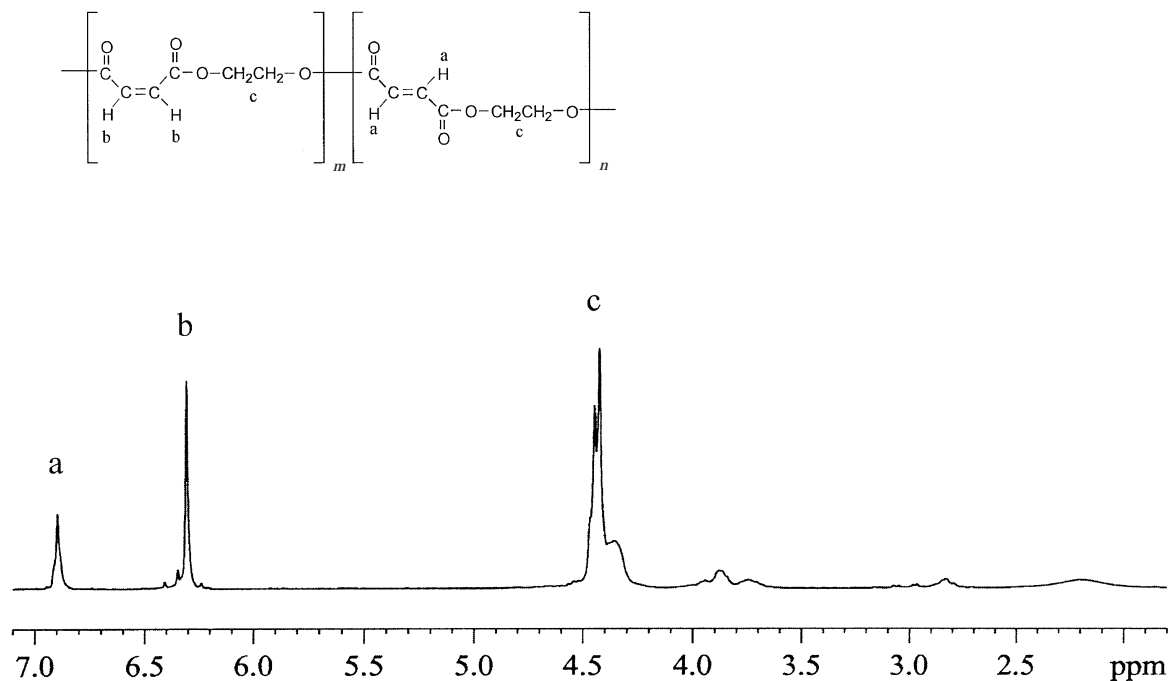
Figure 1. ^{1}H NMR spectrum of poly(MAn-*co*-EG) (**3a**, run 6) in CDCl$_3$.
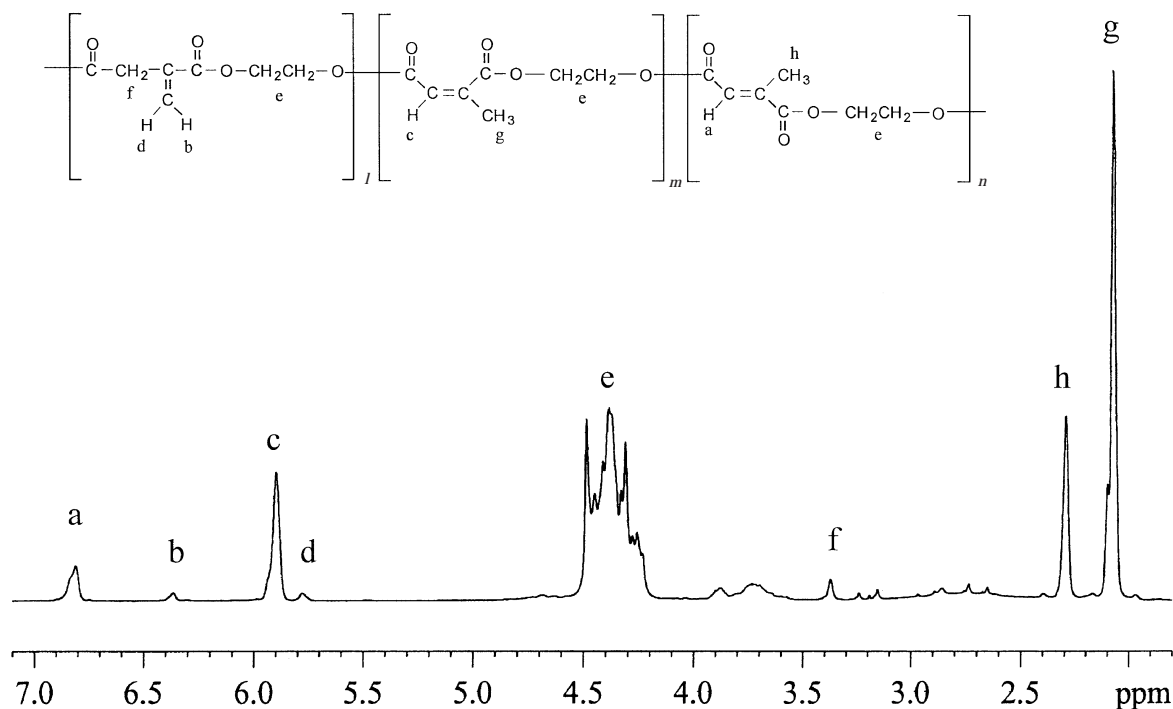

Figure 2. ^{1}H NMR spectrum of poly(CAn-*co*-EG) (**4a**, run 9) in CDCl$_3$.

ability of the sample would not be influenced so much by such a level of EG–EG linkage.

Poly(CAn-*co*-EG) (**4a**) was synthesized under the same condition as that of **3a** except for amount of solvent. For the synthesis of poly(CAn-*co*-EG) (**4a**) with high molecular weight, it was also required to reduce the amount of solvent. Figure 2 shows ^{1}H NMR spectrum of the polymer **4a**(run 9).

Two peaks at 6.81 ppm due to methine proton and at 2.29 ppm due to methyl proton of *E*-configuration were found clearly, indicating that *Z*- to *E*-isomerization occurred during polycondensation. This isomerization could be confirmed by the corresponding ^{13}C NMR spectrum. Unexpectedly, three peaks at 6.36, 5.77, and 3.37 ppm assignable to itaconic acid (IA) unit were observed in ^{1}H NMR spectrum, suggesting that not only citraconic (*i.e.*, *Z*-configuration) and mesaconic (*E*-configuration) units but also IA unit were formed
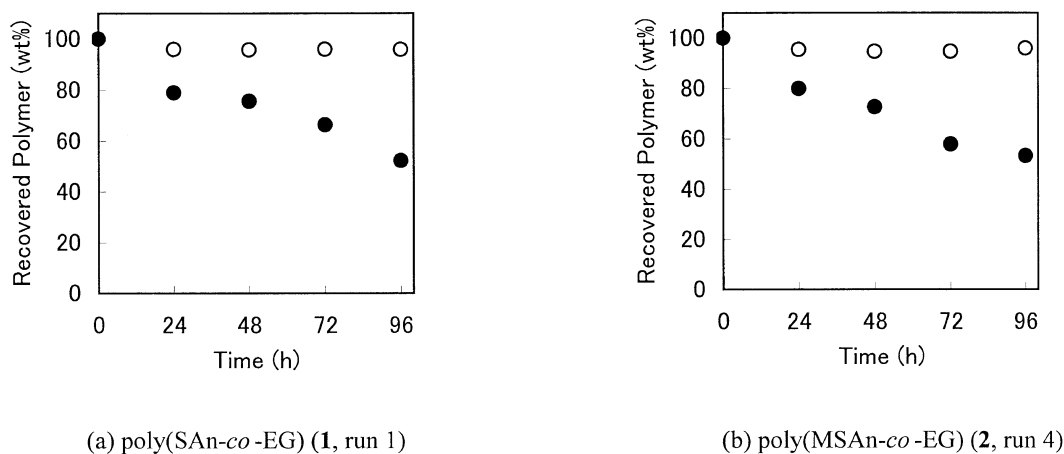
(a) poly(SAn-*co*-EG) (**1**, run 1)   (b) poly(MSAn-*co*-EG) (**2**, run 4)

Figure 3. Enzymatic hydrolysis of saturated polymers; *Rhizopus delemar* (●), and blank (○).

(a) poly(MAn-*co*-EG) (**3a**, run 6)   (b) poly(MAn-*co*-EG) (**3b**, run 7)   (c) poly(FA-*co*-EG) (**3c**, run 8)
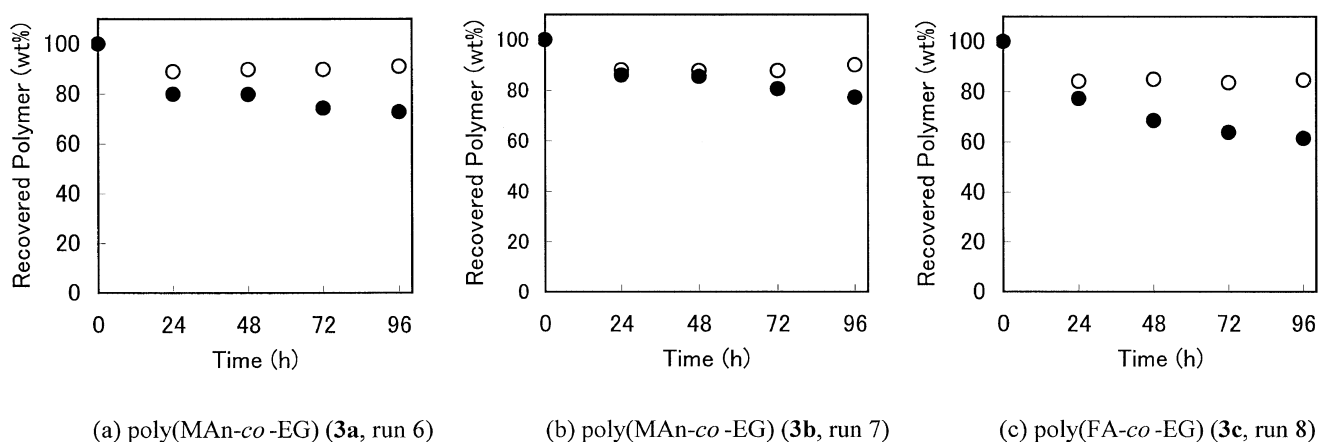
Figure 4. Enzymatic hydrolysis of unsaturated polymers; *Rhizopus delemar* (●), and blank (○).

under the experimental conditions. In contrast with polyester **3a–c** which are stable for more than a few month, **4a** was unstable due to gelation within a few weeks on standing at room temperature. Forming exo-type, *i.e.*, >C=CH$_2$ type, double bond was closely related to gelation of **4a**.

Although polyester **3** and **4** were essentially a linear polymer obtained by solution polycondensation, their molecular weight could not be achieved to $M_n > 10^4$. To obtain high molecular weight polyester, chain extension reaction of polymers with a titanium isopropoxide catalyst was examined.[16, 17] However it resulted in gelation of the polymer prior to the chain extension. For the present, it seems that there are not effective methods except for cross-linking in order to obtain unsaturated polyesters with high molecular weight. However, several works[3, 6, 7] pointed out that the cross-linking resulted in lowering of biodegradability. Therefore non-cross-linked polyester samples (oligomers of $M_n < 4 \times 10^3$) should be employed so as to clarify geometrical effects on their biodegradability.

Enzymatic Degradation Test

The biodegradability of polyester **1, 2,** and **3a–c** was evaluated from enzymatic degradation tests using *Rizopous delemar* lipase at 37°C. Figures 3 and 4 represent the relationship between the weight of the recovered samples and the time course in an enzymatic degradation test.

In comparison with blank test (○), in which only the chemical degradation hydrolysis occurs in phosphate buffer solution at pH 5.6, all samples degraded more readily in the presence of the enzyme in the same buffer solution. In the biodegradation process of polyester **1** and **2** by *Rhizopus delemar*, however, so clear influences of the methyl side chain could not be observed. On the other hand, as for geometric structure of unsaturated units, polyester **3c** which was 100% *E*-configuration degraded more efficient than polyester **3a**, and **3b**.

Biochemical Oxygen Demand Test

Biochemical oxygen demand (BOD) values of the above samples in the presence of activated sludge were
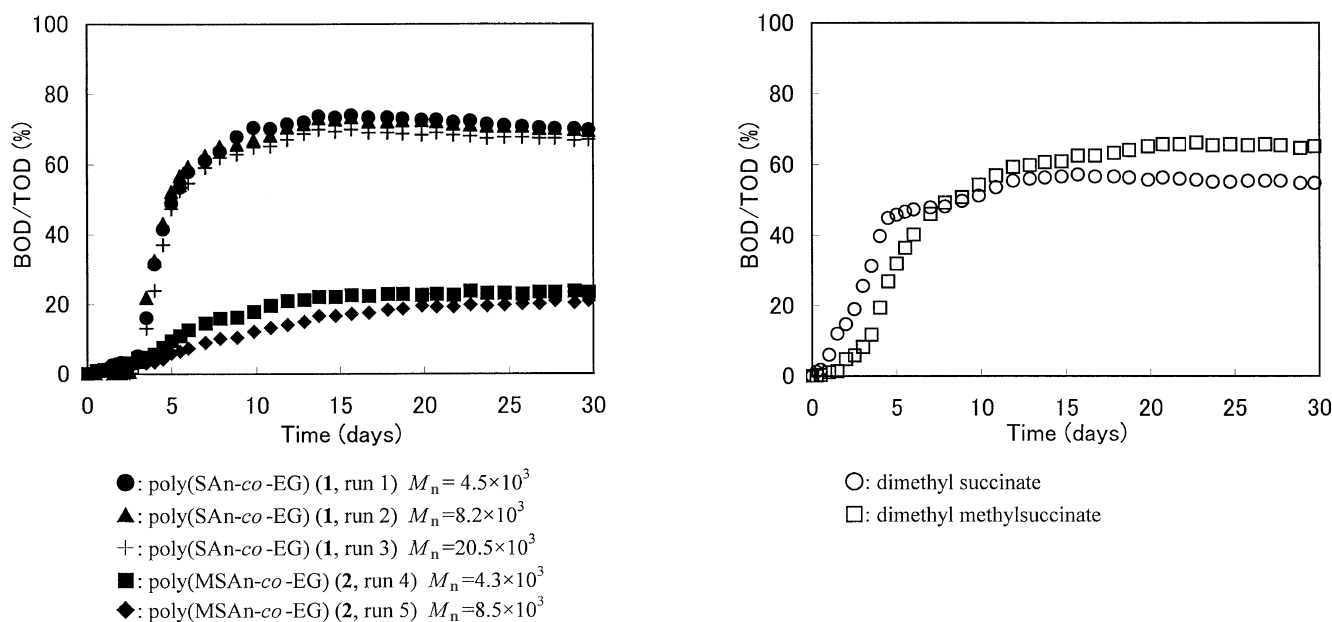
●: poly(SAn-*co*-EG) (**1**, run 1) $M_n = 4.5 \times 10^3$
▲: poly(SAn-*co*-EG) (**1**, run 2) $M_n = 8.2 \times 10^3$
+: poly(SAn-*co*-EG) (**1**, run 3) $M_n = 20.5 \times 10^3$
■: poly(MSAn-*co*-EG) (**2**, run 4) $M_n = 4.3 \times 10^3$
◆: poly(MSAn-*co*-EG) (**2**, run 5) $M_n = 8.5 \times 10^3$

○: dimethyl succinate
□: dimethyl methylsuccinate

Figure 5. Biodegradability of saturated polyesters and model compounds evaluated by biochemical oxygen demand (BOD).

●: poly(MAn-*co*-EG) (**3a**, run 6)
▲: poly(MAn-*co*-EG) (**3b**, run 7)
■: poly(FA-*co*-EG) (**3c**, run 8)

○: dimethyl malate (*Z*-configuration model)
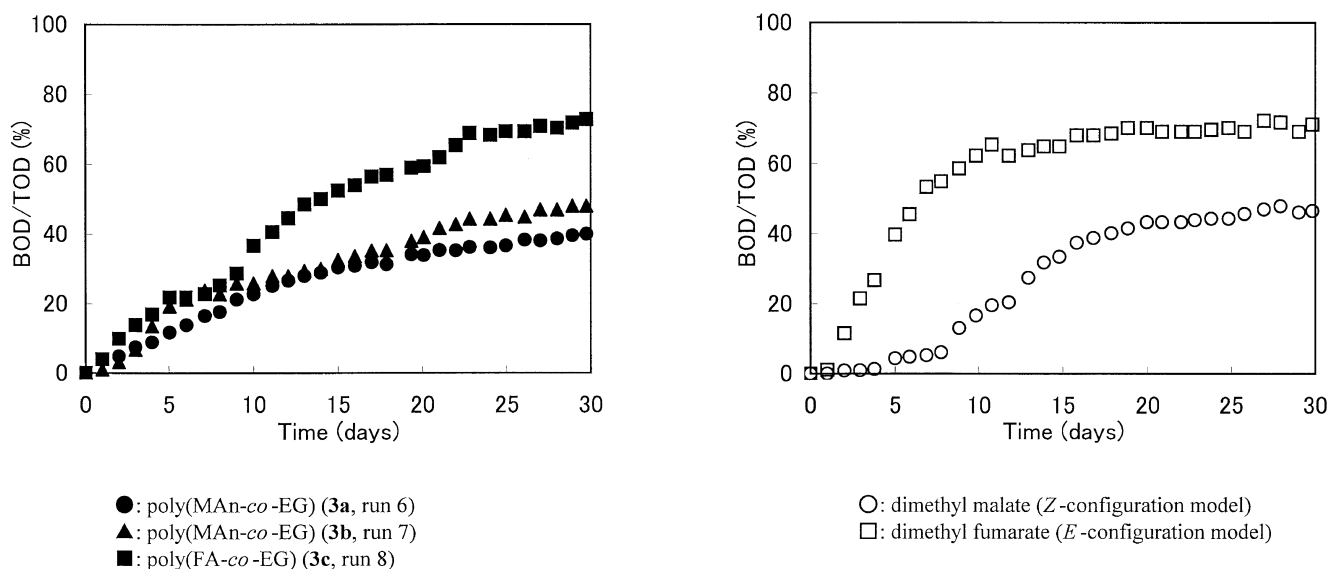□: dimethyl fumarate (*E*-configuration model)

Figure 6. Biodegradability of unsaturated polyesters and model compounds evaluated by biochemical oxygen demand (BOD).

measured with a BOD tester using the oxygen consumption method for 30 days. In addition to polymer samples, BOD values of dimethyl esters derived from the corresponding acids, succinic, methylsuccinic, maleic, and fumaric acid were measured in order to investigate the biodegradability of the repeating unit. These dimethyl esters are used as model compounds in this paper.

Figure 5 shows the ratio BOD/TOD (TOD: theoretical oxygen demand) curves against reaction times. Dimethyl succinate (○) began to degrade instantly and reached to 60% after 10 days. Even though somewhat longer induction period was found in the case of dimethyl methylsuccinate ( ), the degree of degradation after 10 days was reached to almost the same

value as that of dimethyl succinate. For polymer sample, however, it seems that the methyl group prevents efficient biodegradation of the samples. This behavior is different from the result in enzymatic degradation tests of polyester **1** and **2** described above. This discrepancy might be based on the difference in both evaluation methods. Enzymatic degradation tests reflect only by hydrolysis of polymers, whereas BOD values obtained above reflect not only hydrolysis but also metabolism of microorganisms in an activated sludge. It should be noted that the rate of biodegradation of the samples tended to be slower as their molecular weight was higher. This allows us to speculate that a longer chain of polymer makes its biodegradability lower even though the repeating unit of the polymer, *i.e.*, model

compound, is subject to biodegradation. The presence or absence of methyl group is not a direct reason to determine the degradation rate, since the retardation effect due to methyl groups is observed only when they were placed along the polymer main chain.

Figure 6 shows the BOD/TOD values for unsaturated polyester samples and their model compounds. Dimethyl maleate ( ) and fumarate ( ) were gradually degraded to about 40 and 60% after 30 days, respectively. It is interesting that the biodegradation of dimethyl fumarate (all *E*-model) is considerably faster than dimethyl maleate (all *Z*-model). Similar behavior was observed among samples (**3a**–**c**) composed of different molar fractions of *Z*-/*E*-configuration. In comparison with saturated polyester **1** and **2**, unsaturated ones prevent their efficient biodegradation, especially in the case of *Z*-configuration rich polyester. It was revealed that the simplest model compound, which corresponds to the repeating unit of polymer, is essentially subject to biodegradation even though it contains C=C bond. In fact, the biodegradability of *E*-configuration model (dimethyl fumarate) showed almost the same behavior as that of the saturated model (dimethyl succinate). On the other hand, the *Z*-model (dimethyl maleate) was not done so effectively as the *E*-model. Such the specific difference due to the geometric configuration of the double bond was observed again for the polymer samples. As the chain length of polyester having the double bond was longer, however, its biodegradability became lower. The biodegradation rate can be controlled well by the introduction of double bond in the polymer chain, depending on its *Z*-/*E*-configuration ratio.

CONCLUSION

In this paper, unsaturated aliphatic polyesters (**3** and **4**) and saturated ones (**1** and **2**) were synthesized by solution and melt polycondensation method, respectively. The effect of C=C double bond as well as methyl group involved in the polyester samples on their biodegradability has been investigated by enzymatic degradation test using *Rizopous delemar* lipase, and measurement of biochemical oxygen demand (BOD) values in an ac-

tivated sludge. In comparison with saturated polyester, unsaturated ones prevented their efficient biodegradation especially by introducing *Z*-configuration of double bond in the polymer. However, *E*-configuration did not affect so remarkably. The biodegradability of the aliphatic polyester suppressed by introducing methyl group, even if both the model compounds with and without methyl group degrade easily.

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