

Synthesis of Biodegradable Polyesters by Ring-Opening Copolymerization of Cyclic Anhydrides Containing a Double Bond with 1, 2-Epoxybutane and One-Pot Preparation of the Itaconic Acid-Based Polymeric Network

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ABSTRACT: Ring-opening copolymerizations of itaconic anhydride (IAN) or citraconic anhydride (CAN) with 1,2-epoxybutane (EB) were carried out using aluminium triisopropoxide ($\text{Al}(\text{O}^i\text{Pr})_3$) and magnesium diethoxide ($\text{Mg}(\text{OEt})_2$). The resulting copolymers were characterized for molar composition and sequences by FT-IR, ^1H and ^{13}C NMR spectra. The copolymers obtained using $\text{Al}(\text{O}^i\text{Pr})_3$ initiator were found to contain homosequences of EB, *i.e.*, copolyesterethers (**1a** and **2a**), while those produced by $\text{Mg}(\text{OEt})_2$ were alternating copolymers, *i.e.*, polyesters (**1b** and **2b**), irrespective of various feed monomer ratio. Differential scanning calorimetry analysis of the copolymers revealed a relationship between the glass transition temperature and the structure. One-pot preparation of itaconic acid-based highly cross-linked polymer was achieved through cleavage of exo-type double bond of IAN unit in the copolymers. Enzymatic degradation test for the films of cross-linked poly(IAN-co-EB) by *Pseudomonas* sp. and *Rhizopus delemar* lipase indicated that EB homosequence aided the enzymes to access the ester linkage in the cross-linked copolymers. The cross-linked poly(IAN-co-EB) films degraded moderately for 120 days in soil.

KEY WORDS Biodegradable Polyester / Ring-Opening Copolymerization / Itaconic Anhydride / Citraconic Anhydride / 1, 2-Epoxybutane / Alternating Copolymer / Cross-Linked Polymer /

Development of biodegradable polymers is of great importance, since environmental pollution due to plastic wastes has become more increasingly serious. Among synthetic polymers, aliphatic polyesters are generally susceptible to biological attack.¹⁻³ Effective utilization of abundant natural resources as precursors for the production of polymeric materials is needed from the standpoint of preservation of limited mineral oil.⁴ Therefore, molecular design of biodegradable polymers using natural resources as precursors is essential. Okada *et al.* reported syntheses and biodegradabilities of carbohydrate-based polyesters.⁵⁻⁷ We studied the synthesis of alternating copolymers, *i.e.*, poly(butadiene-*alt*-methyl methacrylate),⁸ poly(ethylene-*alt*-methyl methacrylate),⁹ poly(ethylene-*alt*-methacrylonitrile),¹⁰ poly(ethylene-*alt*-vinyl alcohol),¹¹ poly(ethylene-*alt*-vinyl acetate),¹¹ and poly(propylene-*alt*-methyl methacrylate).¹² Although synthesis of biodegradable polyester by ring-opening alternating copolymerization of succinic anhydride with ethylene oxide has already been reported by Maeda *et al.*,¹³ we have been interested in the synthesis of other biodegradable alternating copolymers.

Itaconic acid is present in some fungi (*Aspergillus terreus*, *A. itaconicus*, etc.). Commercially, itaconic acid is produced by the cultivation of *Aspergillus terreus* with molasses or glucose.¹⁴ Recently, more than 60 g L^{-1} of itaconic acid have been obtained by the same cultivation with corn starch.¹⁵ Therefore, itaconic acid is one of interesting natural resources for industrial production of biodegradable polymeric materials.

In the present paper, ring-opening copolymerizations of itaconic anhydride (IAN) and citraconic anhydride (CAN) with 1,2-epoxybutane (EB) were examined using aluminium triisopropoxide ($\text{Al}(\text{O}^i\text{Pr})_3$) or magnesium diethoxide ($\text{Mg}(\text{OEt})_2$) as initiator for exploration of new biodegradable polyesters and an effective utilization of itaconic acid. To the best of our knowledge, the synthesis of itaconic acid-based polyesters has not been reported until now. Furthermore, one-pot preparation of cross-linked copolymer was carried out through the cleavage of exo-type double bond in IAN unit with the aim at improving the mechanical properties of the copolymer.

EXPERIMENTAL

Materials

IAN and CAN were kindly supplied by Iwata Chemical Co., Ltd. (Shizuoka, Japan). EB and Aluminium triisopropoxide ($\text{Al}(\text{O}^i\text{Pr})_3$) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Magnesium diethoxide ($\text{Mg}(\text{OEt})_2$) (Kanto Chemical Co., Inc., Tokyo) was used for the preparation of the polymers. Toluene, chloroform (CHCl_3), *n*-hexane used were purified by distillation.

Measurement

FT-IR spectra were recorded in KBr using a JASCO FT/IR-430 spectrometer and a 100% KBr disk was used as blank. ^1H and ^{13}C NMR spectra were taken on a Varian UNITY PLUS400 (400 MHz for ^1H) or a JEOL JNM-GX400 (400 MHz for ^1H) in CDCl_3 at room temperature. All chemical shifts were expressed as δ from tetramethylsilane (TMS). Number average molecular

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weight (M_n) and polydispersity (M_w/M_n) of the polyesters were determined by size-exclusion chromatography (SEC) calibrated with polystyrene standards using a system of Tosoh HLC 803D with a Tosoh RI-8020 detector and Tosoh G2000-, G3000-, G4000-, and G5000-HXL columns (eluent: tetrahydrofuran, temperature: 40°C). Differential scanning calorimetry (DSC) was determined on a Seiko I TA Station with a DSC 210 unit from -150 to 200°C at a heating rate of 10°C min⁻¹, calibrated with indium and tin. A sample weighing between 4 and 6 mg was taken in an aluminium pan with a lid. T_g was taken at the inflection point of the corresponding heat capacity jump, and T_m was measured as the onset of the melting peak of DSC trace. Solid state ¹³C cross polarization magic angle spinning (CP-MAS) NMR spectra were collected on a Varian UNITY PLUS400 (100 MHz for ¹³C) spectrometer at room temperature. The spinning rate, 90° pulse width for ¹H, and contact and repetition times were 5 kHz, 4.5 μs, 2 ms, and 5 s, respectively. Surfaces of the films after enzymatic degradation and soil burial tests were observed with JEOL JSM-5200 scanning electron microscope (SEM). Tensile strength and elongation at break of the films (30 × 5 × 0.5 mm) were evaluated using a Toyo Baldwin Tensilon UTM-III-20 testing machine with a cross-head speed of 10 mm min⁻¹ at room temperature. The values are means of 3–5 samples.

Synthesis of Poly(IAn-co-EB) (1)

A typical experimental procedure is as follows. A mixture of 0.84 g (11.6 mmol) of EB and 1.30 g (11.6 mmol) of IAn was dissolved in 2.9 mL of toluene at room temperature under nitrogen atmosphere. This mixture was polymerized by addition of 0.0873 mmol of Mg(OEt)₂. After stirring at 80°C for 120 h, the mixture was diluted with CHCl₃ and inorganic components were extracted with water containing a trace amount of HCl. The organic solution was poured into *n*-hexane, and the supernatant was removed by decantation. After reprecipitation from CHCl₃ solution into *n*-hexane as a non-solvent, the polymeric material was collected and dried *in vacuo* to give waxy solid **1b** (55.6% yield, run 7 in Table I).

IR (KBr disk) 2972 (ν_{C-H}), 1769, 1733 ($\nu_{C=O}$ (ester)), 1653 ($\nu_{C=C}$), 1457, 1446 (δ_{C-H}), 1178 cm⁻¹ (ν_{C-O-C} (ester)).

¹H NMR (CDCl₃, 1.0 wt%, 27°C, TMS) δ 6.34 (CH=CH₂), 5.85 (CH=C), 5.75 (CH=CH₂), 5.21–4.85 (CH₂CHO), 4.50–3.98 (CH₂CHO), 3.34 (COCH₂), 2.10–2.01 (CH₃C), 1.82–1.40 (CH₃CH₂), 1.06–0.81 ppm (CH₃CH₂).

¹³C NMR (CDCl₃, 5.0 wt%, 27°C, TMS) δ 171.0 (COCH₂), 168.7 (CCOO(CAn unit)), 166.0 (CCOO(IAn unit)), 165.7 (COCH), 147.0–146.0 (C=CH), 134.2 (C=CH₂), 129.0 (C=CH₂), 120.5 (C=CH), 74.5–73.0 (CH₂CHO), 66.0–64.5 (CH₂CHO), 37.5 (COCH₂), 23.2 (CH₃CH₂), 20.8 (CH₃C), 9.5 ppm (CH₃CH₂).

Synthesis of Poly(CAn-co-EB) (2)

The preparative method was similar to that of copolymer **1**, described above. Yield, 79.3% (run 9 in Table II).

IR (KBr disk) 2973 (ν_{C-H}), 1729 ($\nu_{C=O}$ (ester)), 1653

($\nu_{C=C}$), 1445 (δ_{C-H}), 1173 cm⁻¹ (ν_{C-O-C} (ester)).

¹H NMR (CDCl₃, 1.0 wt%, 27°C, TMS) δ 5.85 (CH=C), 5.27–4.98 (CH₂CHO), 4.40–4.08 (CH₂-CHO), 2.13–2.01 (CH₃C), 1.80–1.58 (CH₃CH₂), 1.07–0.85 ppm (CH₃CH₂).

¹³C NMR (CDCl₃, 5.0 wt%, 27°C, TMS) δ 168.5 (CCOO), 164.5 (COCH), 147.0–146.0 (C=CH), 121.10–119.8 (C=CH), 74.0, 73.0 (CH₂CHO), 66.0–63.5 (CH₂CHO), 23.2 (CH₃CH₂), 20.8 (CH₃C), 9.6 ppm (CH₃CH₂).

One-Pot Preparation of Cross-Linked Poly(IAn-co-EB)

One-pot preparation of cross-linked copolyesterether and polyester was carried out using Al(O^{*i*}Pr)₃ and Mg(OEt)₂, respectively. A typical run of the successive cross-linked poly(IAn-co-EB) synthesis is follows. The first step was the polymerization of IAn and EB. To a mixture of 3.0 mL of toluene, 6.50 g (58.0 mmol) of IAn, and 4.18 g (58.0 mmol) of EB in a glass tube was added 0.05 g (0.44 mmol) of Mg(OEt)₂ at room temperature. The tube was sealed and kept at 80°C for 48 h, which might be enough long time to complete polymerization. Then, the tube was transferred to an oil bath heated at 120°C. The gelation took place within 24 h. After 72 h, the gel was immersed in CHCl₃ to remove unreacted chemicals by filtration. The soluble fraction in CHCl₃ of the polymeric products was found to be 11.6%. The insoluble part was dried in a vacuum oven at 50°C for 24 h (61.6% yield, run 2 in Table III).

IR (KBr disk) 2972 (ν_{C-H}), 1769, 1734 ($\nu_{C=O}$ (ester)), 1653 ($\nu_{C=C}$), 1458 (δ_{C-H}), 1176 cm⁻¹ (ν_{C-O-C} (ester)).

¹³C CP-MAS NMR (27°C) δ 170.8–160.5 (COCH₂, CCOO(CAn unit), CCOO(IAn unit), COCH), 141.0–124.0 (C=CH, C=CH₂, C=CH₂), 121.0–118.5 (C=CH), 89.5–58.5 (CH₂CHO, CH₂CHO), 54.0–42.5 (CH₂C, CH₂C (cross-links)), 42.5–30.4 (COCH₂), 30.0–16.2 (CH₃CH₂, CH₃C), 14.0–6.0 ppm (CH₃-CH₂).

Enzymatic Degradation

Enzymatic hydrolysis was carried out as follows. Cross-linked polyesterether or polyester film (thickness: 0.5 mm) were prepared from the powder by a melt-press (Shintou Kinzoku Kogyo, Co.) at 220°C under a pressure of 0.01 kg m⁻². 30 mg of the network film (10 × 5 × 0.5 mm) and 2.0 mL of phosphate buffer (KH₂PO₄/K₂HPO₄, pH 7.0) were placed in a test tube, and 25 units of the enzyme were added. A blank test was conducted for the polymer film in the same phosphate buffer without the enzyme. The enzymatic tests were carried out for a fixed time. The recovered sample was washed with water, dried to a constant weight under reduced pressure. The recovered sample weight in the text are the mean of 3 samples.

Soil Burial Degradation (Field Test)

Cross-linked copolyesterether films (30 × 5 × 0.5 mm) were buried in a field (under 15 cm from the surface) of Mikawa Textile Research Institute in Gamogori city. After designated times, the films were dug out, washed with water, and dried to a constant weight under reduced pressure. To be more accurate, three sheets of the same sample were tested simultaneously and all data were

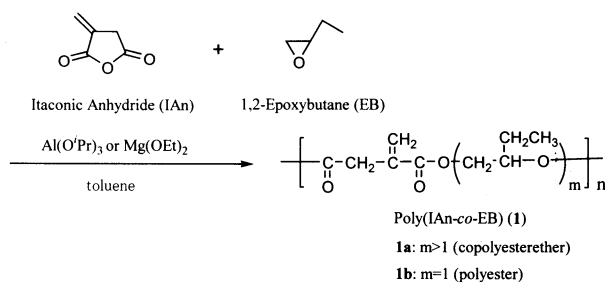
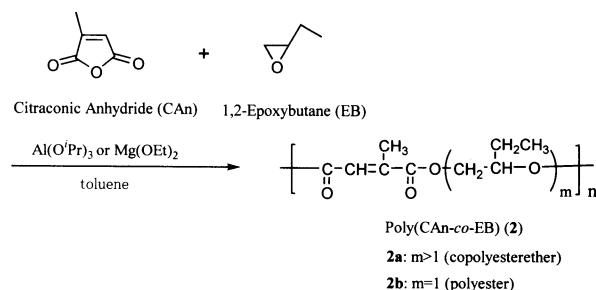

Scheme 1. Ring-opening copolymerization IAn with EB.

Scheme 2. Ring-opening copolymerization CAn with EB.

Table I. Ring-opening copolymerization of IAn with EB using $\text{Al}(\text{O}^i\text{Pr})_3$ or $\text{Mg}(\text{OEt})_2$ ^a

Run	Initiator	[IAn] ₀ /[EB] ₀ ^b	Time h	Yield/%		$M_n^d \times 10^{-4}$	M_w/M_n^d	m_1/m_2^e mol%	IAn/CAn ^f mol%	Z^g mol%
				Soluble ^c	Insoluble ^c					
1	$\text{Al}(\text{O}^i\text{Pr})_3$	1/1	120	7.2	46.0	0.27	1.9	36/64	60/40	28
2	$\text{Al}(\text{O}^i\text{Pr})_3$	1/2	120	47.9	13.1	0.31	2.0	41/59	47/53	35
3	$\text{Al}(\text{O}^i\text{Pr})_3$	0/1	120	48.0	0	5.02	1.7	—	—	—
4	$\text{Mg}(\text{OEt})_2$	1/1	24	19.5	0	0.07	1.8	48/52	77/23	12
5	$\text{Mg}(\text{OEt})_2$	1/1	48	44.0	0	0.19	2.7	48/52	59/41	14
6	$\text{Mg}(\text{OEt})_2$	1/1	72	49.9	0	0.33	3.3	49/51	42/58	19
7	$\text{Mg}(\text{OEt})_2$	1/1	120	55.6	0	0.36	4.7	48/52	40/60	15
8	$\text{Mg}(\text{OEt})_2$	3/1	72	97.3	0	0.14	1.7	48/52	78/22	38
9	$\text{Mg}(\text{OEt})_2$	1/2	72	67.2	0	0.87	7.7	49/51	65/35	29
10	$\text{Mg}(\text{OEt})_2$	1/3	72	64.6	0	0.47	6.3	46/54	59/41	29
11	$\text{Mg}(\text{OEt})_2$	0/1	120	—	—	—	—	—	—	—

^a [IAn]₀ = [EB]₀ = 5.6 mol L⁻¹; [IAn]₀ + [CAn]₀/[I]₀ = 264; solv., toluene; temp, 120°C (run 1, 2, and 11), 80°C (run 3—10). ^b Feed molar ratio of IAn to EB. ^c Soluble or insoluble part of reaction mixture. ^d Determined by SEC in THF (polystyrene standards). ^e Molar ratio of IAn and CAn (m_1) unit to EB (m_2) unit in polymer, determined by ¹H NMR in CDCl₃. ^f Molar ratio of IAn unit to CAn unit in polymer, determined by ¹H NMR in CDCl₃. ^g Degree of cross-linking of soluble part of the reaction mixture.

averaged.

RESULTS AND DISCUSSION

Synthesis of Poly(IAn-co-EB) (1)

According to Scheme 1, ring-opening copolymerization of IAn and EB was examined in toluene at various monomer ratios ([IAn]₀/[EB]₀) by using both $\text{Al}(\text{O}^i\text{Pr})_3$ and $\text{Mg}(\text{OEt})_2$ as initiators (Table I).

A key feature in such a polymerization is the use of metallic alkoxides in catalytic amount so as to minimize complexation (0.038 mol L⁻¹).¹⁶ Both initiators underwent copolymerization of IAn and EB. The yields of the copolymers increased with reaction time (run 4—7). Figures 1a and 1b show ¹H NMR spectra of the typical poly(IAn-co-EB)s synthesized by using $\text{Al}(\text{O}^i\text{Pr})_3$ and $\text{Mg}(\text{OEt})_2$, respectively. In only the former case, however, solidification of the polymerization mixture was observed after 24 h at 120°C, which seemed to be due to cross-linking of the polymer. The occurrence of intermolecular cross-linking was supported by appearance of peaks at 2.95—2.60 ppm assigned to methylene protons generated by the cleavage of exo-type double bonds in IAn unit (Figure 1a). In all cases, peaks ascribed to methyl protons (2.10—2.01 ppm) and methine protons (5.85 ppm) of CAn units were observed unexpectedly, indicating that the isomerization from IAn unit into CAn unit occurred under the experimental conditions. The molar ratios of IAn unit to CAn unit (IAn/CAn) were 78/22—40/60 and the CA content in the copolymers was

increased with the reaction time. The molar ratios of IAn and CAn unit to EB unit in the copolymers (m_1/m_2), determined by ¹H NMR intensity ratios of peaks b, c (IAn units), and peak d (CAn units) to peaks f, g, and j (EB units) (see Figure 1a), depends on initiator. In the case of $\text{Al}(\text{O}^i\text{Pr})_3$, m_1/m_2 was 36/64—41/59, indicating that the copolymers had always homosequences of EB (copolyesterether **1a**). In the ¹H (Figure 1a) and ¹³C NMR spectra of the copolymer, peaks at 3.75—3.30 ppm for ¹H and at 71.0 and 70.0 ppm for ¹³C NMR spectrum were observed. These chemical shifts were identified with those of homopolymer obtained by ring-opening polymerization of EB with $\text{Al}(\text{O}^i\text{Pr})_3$ initiator (run 3 in Table I). The simplicity of the ethyl signals assigned to homosequence of EB in the ¹³C NMR spectrum indicates that the EB homosequence in copolymer **1** consists exclusively of head-to-tail linkages.¹⁷ No peaks ascribed to homosequence of EB could be observed in copolymers produced by $\text{Mg}(\text{OEt})_2$ initiator (see Figure 1b) and m_1/m_2 was almost 50/50 irrespective of the feed molar ratio [IAn]₀/[EB]₀ (run 6 and 8—10 in Table I). This was supported by the result that $\text{Mg}(\text{OEt})_2$ did not undergo the homopolymerization of EB at 120°C (run 11 in Table I). There is no evidence for homosequences of IAn or CAn in IR, ¹H, and ¹³C NMR spectra. The results reveal that the copolymers are alternating copolymers, namely the polyester **1b**.

Synthesis of Poly(CAn-co-EB) (2)

Poly(CAn-co-EB) (**2**) was synthesized by the ring-

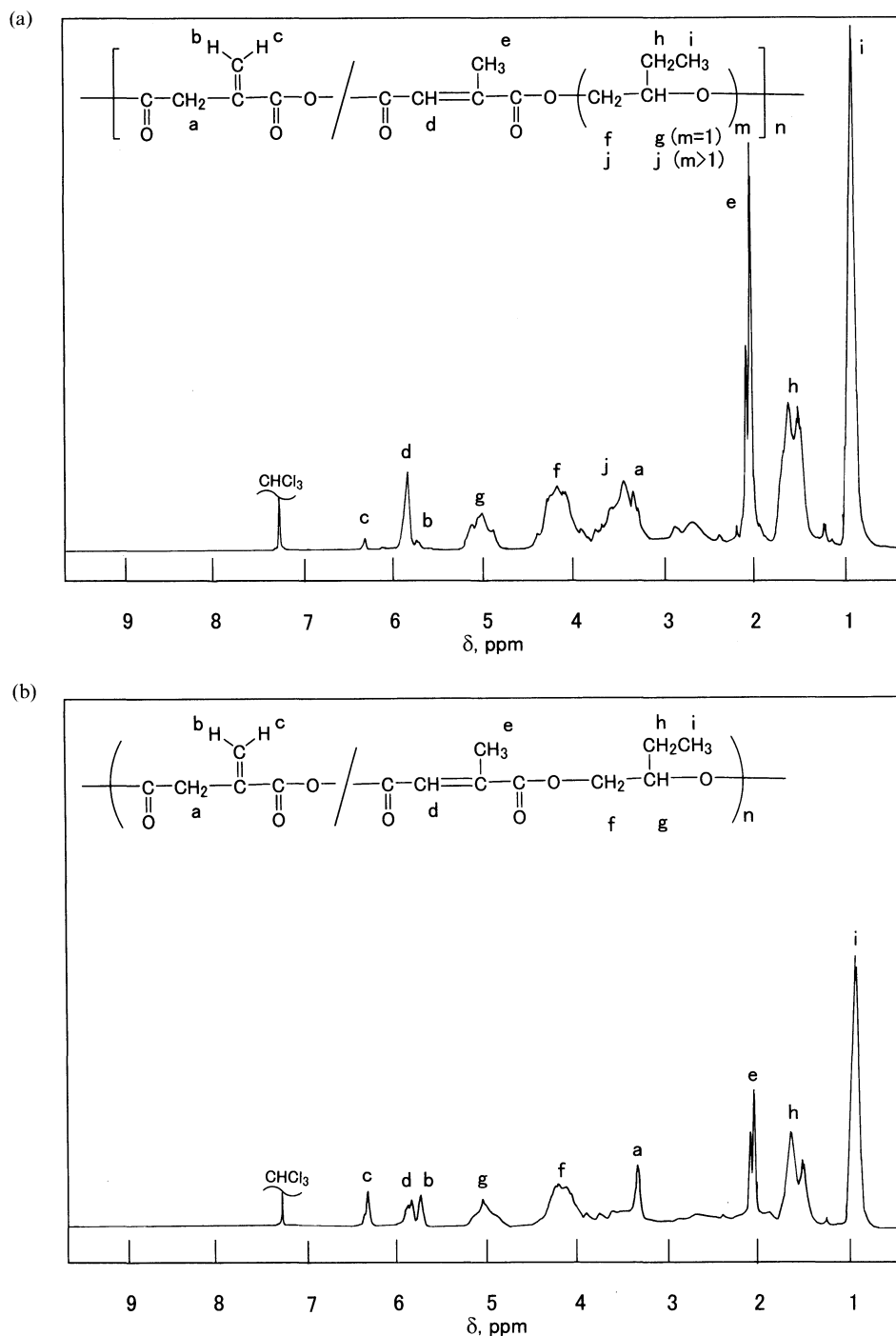


Figure 1. ^1H NMR spectra of poly(IAN-*co*-EB) (1) synthesized using $\text{Al}(\text{O}^i\text{Pr})_3$ (a) and $\text{Mg}(\text{OEt})_2$ (b) in CDCl_3 at 27°C .

opening copolymerization of CAN and EB under the same conditions as copolymerization of IAN and EB (Table II).

The reaction proceeded homogeneously even at 120°C , suggesting the absence of cross-linking. ^1H NMR spectra of the resulting copolymers initiated with $\text{Al}(\text{O}^i\text{Pr})_3$ and $\text{Mg}(\text{OEt})_2$ are shown in Figures 2a and 2b, respectively. No cross-links through the cleavage of endo-type double bond in the polymer was observed in the both ^1H and ^{13}C NMR spectra. This is readily expected by the reason that the endo-type double bond in the copolymer **2** is less reactive than the exo-type double bond in the copolymer **1**, because the former is trisubstituted and the latter is disubstituted. The molar ratios of CAN unit to

EB unit in the copolymers (CAN/EB) were determined by ^1H NMR intensity ratios of methine protons of CAN units at 5.85 ppm to methylene protons of EB units at 4.40–4.08 ppm and methylene protons of EB units in the homosequence at 3.75–3.30 ppm.

Molecular weights obtained from SEC measurement were 0.15×10^4 – 0.64×10^4 , which were different from those expected ($M_n = 33900$) from the feed monomer to initiator ratio $[(\text{CAN})_0 + (\text{EB})_0]/[\text{I}]_0 = 265$. Observed M_n increased gradually for 120 h, accompanied with a subtle broadening of molecular weight distribution (run 2–4 and 7–9). Intermolecular transesterification might cause a decrease of the M_n of produced polymer and broadening of the molecular weight distribution.

Table II. Ring-opening copolymerization of CAn with EB using Al(OⁱPr)₃ or Mg(OEt)₂^a

Run	Initiator	[CAn] ₀ [EB] ₀ ^b	Temp	Time	Yield	$M_n^c \times 10^{-4}$	m_w/M_n^c	m_1/m_2^d
			°C	h	%			mol%
1	Al(O ⁱ Pr) ₃	1/1	120	120	60.1	0.43	2.5	41/59
2	Al(O ⁱ Pr) ₃	1/1	80	24	54.2	0.37	1.7	42/58
3	Al(O ⁱ Pr) ₃	1/1	80	72	74.0	0.56	2.0	43/57
4	Al(O ⁱ Pr) ₃	1/1	80	120	82.0	0.48	2.3	43/57
5	Al(O ⁱ Pr) ₃	1/2	80	72	59.3	0.36	2.1	42/58
6	Al(O ⁱ Pr) ₃	1/3	80	72	51.2	0.41	1.6	41/59
7	Mg(OEt) ₂	1/1	80	24	2.1	0.15	1.6	48/52
8	Mg(OEt) ₂	1/1	80	72	51.1	0.33	1.8	50/50
9	Mg(OEt) ₂	1/1	80	120	79.3	0.38	2.4	49/51
10	Mg(OEt) ₂	3/1	80	72	34.1	0.09	1.6	49/51
11	Mg(OEt) ₂	1/3	80	72	41.5	0.46	2.3	47/53

^a[IAN]₀=[EB]₀=5.6 mol L⁻¹; [CAn]₀/[I]₀=265; [I]₀=0.038 mol L⁻¹; solv., toluene. ^bFeed molar ratio of CAn to EB. ^cDetermined by SEC in THF (polystyrene standards). ^dMolar ratio of CAn (m_1) unit to EB (m_2) unit in polymer, determined by ¹H NMR in CDCl₃.

Chain-extension reactions using titanium iso-propoxide¹⁸ as catalyst for the original polyester **2b** (M_n =3300, run 8 in Table II) resulted in the polyester having M_n of 5300. Thus, the efficient chain-extension seemed to be difficult.

One-Pot Preparation of Cross-Linked Poly(IAn-co-EB)

Cross-linked copolyesterether and polyester were prepared in one-pot procedure using Al(OⁱPr)₃ and Mg(OEt)₂, respectively. After conventional copolymerization of IAn and EB at 80°C for 48 h, elevation of reaction temperature up to 120°C brought about gelation. The results are summarized in Table III.

The structures and compositions of the resulting cross-linked samples were confirmed by IR and solid state ¹³C CP-MAS spectra. The IR spectrum of cross-linked copolyesterether was similar to that of the copolyesterether **1a**. ¹³C Solid-state NMR spectroscopy is quite useful for studying the structures of polymeric network and chemical bridges responsible for the cross-links under nondestructive conditions.^{19,20} Figure 3 shows a ¹³C CP-MAS spectrum of the cross-linked polyester (run 2 in Table III). The full resonance assignment was achieved in comparison with the ¹³C NMR spectra of polyester **1b** in solution. The molar ratios of IAn and CAn unit to EB unit (m_1/m_2) in the cross-linked copolymer, estimated by ¹³C CP-MAS NMR peak ratios of peaks a, e, h, and l (carbonyl carbon at 170.8–160.5 ppm) to peaks n and m (methine and methylene carbons of EB units at 89.5–58.5 ppm), were 31/69 for run 1 and 47/53 for run 2, indicating that the former was cross-linked copolyesterether having EB homosequence and the latter was cross-linked polyester mostly composed of alternating sequences. The degree of isomerization of IAn unit to CAn unit (IAN/CAN) in the cross-linked polymer was also determined by the CP-MAS NMR intensity ratio of peak i (methine carbon of CAn unit at 121.0–118.5 ppm) to peaks a, e, h, and l (carbonyl carbon at 170.8–160.5 ppm). IAN/CAN in the cross-linked copolyesterether and polyester were 84/16 and 77/23, respectively. Signals in the 54.0–42.5 ppm region were newly observed, all due to the cross-linked methine and methylene carbons (peak c and d in Figures 3), but none due to polyester **1b**. Therefore,

the degree of cross-linking (Z), defined as a mole percent of cross-linked IAn unit to the total IAn and CAn unit in the cross-linked polymer, was estimated by the peak intensity ratio of peak c and d to peak j, f, g, and i (see Figures 3). Z of both cross-linked copolyesterether and polyester were almost the same (62% and 59%, respectively), but higher than those of soluble part. Z of the soluble copolymer **1**, separated from the cross-linked one in the course of work-up procedure, were 43 and 25% for runs 1 and 2, respectively.

Thermal Properties of Copolymers and Cross-Linked Copolymers

The different sequences and degrees of cross-linking are expected to influence the properties of the copolymers. To check the thermal properties of poly(IAn-co-EB) (**1**), poly(CAn-co-EB) (**2**) and cross-linked copolymers, DSC measurement was conducted (Table IV). Copolymer **1** has T_g and T_m and T_g is affected by m_1/m_2 . T_g decreased with increasing EB content in the polymer, in conformity with expectation that the flexible EB homosequence should lower the T_g . Such flexibility was supported by the fact that homopolymer of EB obtained by Al(OⁱPr)₃ initiator (M_n =50200, M_w/M_n =1.7) had a T_g at -124°C. M_n , IAN/CAN, and Z scarcely affect T_g under the experimental conditions. On the contrary, T_m and ΔH of **1** decrease on increasing Z . In the case of copolymer **2**, it can be seen more clearly that EB content affects the T_g and T_m . T_g and T_m increase with decrease of EB content in the polymer and are independent of M_n in agreement with the result of copolymer **1**. Finally, cross-linked copolyesterether and polyester had T_g at 14 and 18°C, respectively. The difference of 4°C in T_g is interpreted by the EB content in the polymer networks. T_g s of the sufficiently cross-linked copolymers were 7–23°C higher than those of the corresponding copolyesterethers **1a** and polyesters **1b**. These results seem to indicate that the flexibility of polymer chain in an amorphous region falls down with an increase in cross-links. Both highly cross-linked copolymers did not show endothermic peak in the DSC trace, although some flexible copolymers **1** showed small endothermic peaks. The results indicate that crystallization of copolyesterether or polyester segment is inhibited

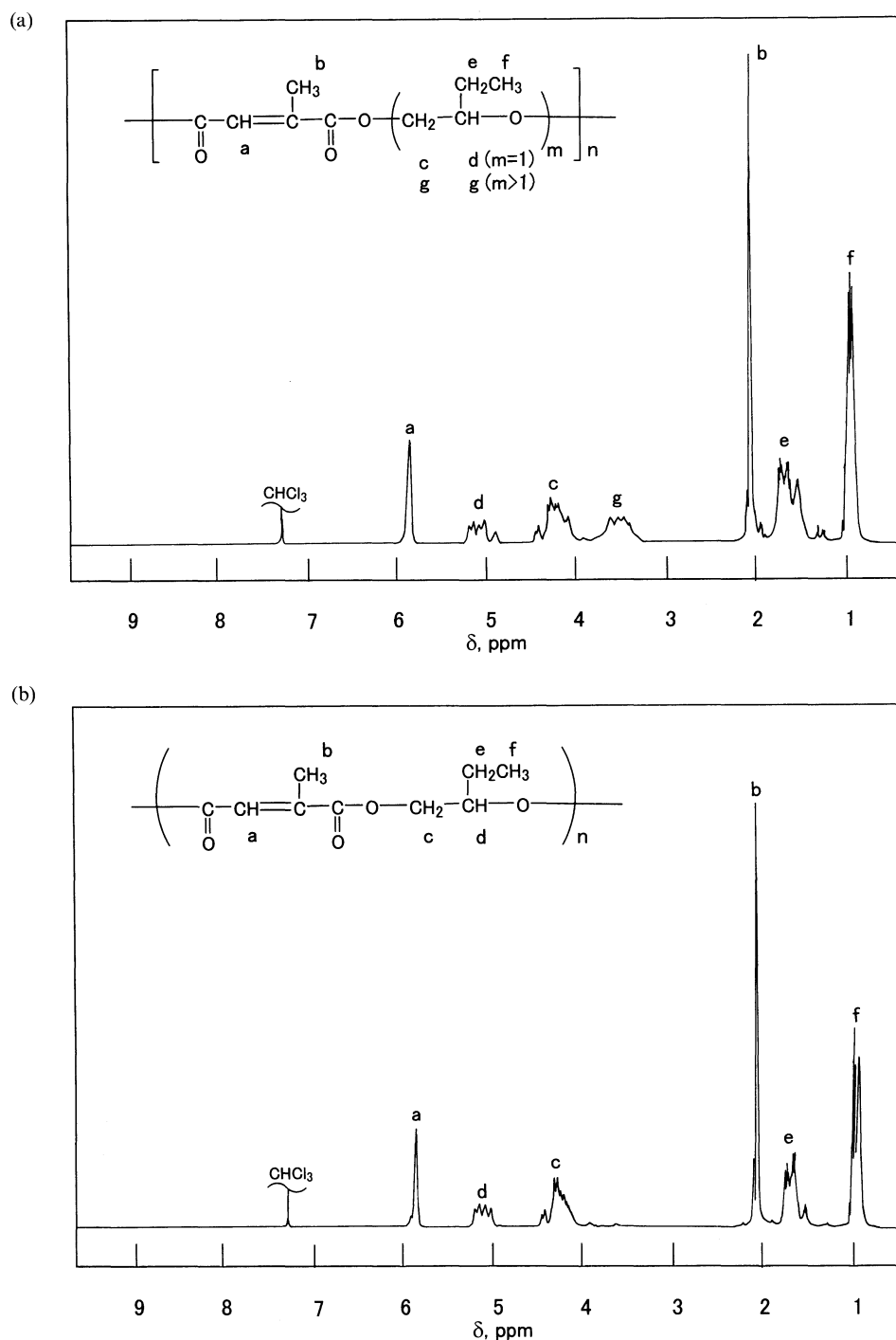


Figure 2. ^1H NMR spectra of poly(CAn-co-EB) (2) synthesized using $\text{Al}(\text{O}^i\text{Pr})_3$ (a) and $\text{Mg}(\text{OEt})_2$ (b) in CDCl_3 at 27°C .

Table III. Preparation of cross-linked poly(IAn-co-EB)^a

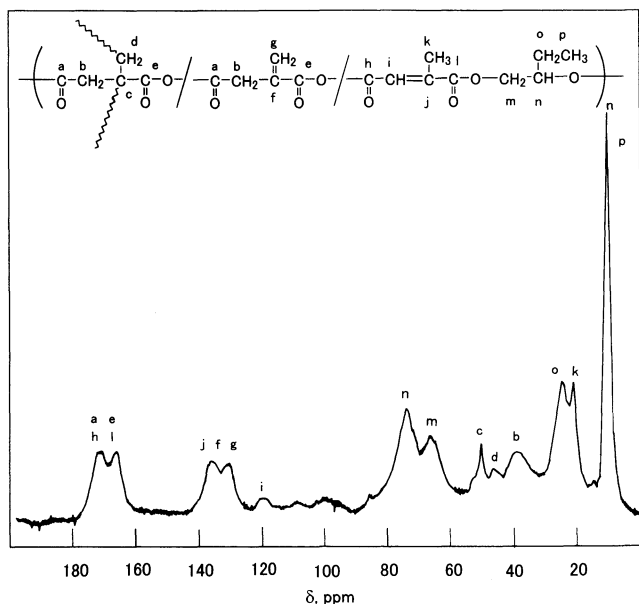
Run	Initiator	Solvent	$[\text{IAn}]_0/[\text{EB}]_0^b$	Yield ^c	m_1/m_2^d	IAn/CAn ^e	Z ^f
				%	mol%	mol%	mol%
1	$\text{Al}(\text{O}^i\text{Pr})_3$	Toluene	1/1	66.9	31/69	84/16	62
2	$\text{Mg}(\text{OEt})_2$	Toluene	1/1	61.6	45/55	77/23	59

^a $[\text{IAn}]_p = [\text{EB}]_0 = 5.6 \text{ mol L}^{-1}$; $([\text{IAn}]_0 + [\text{CAn}]_0)/[\text{I}]_0 = 265$; temp, 80°C (48 h), 120°C (72 h). ^b Feed molar ratio of IAn to EB. ^c Insoluble part of the reaction mixture. ^d Molar ratio of IAn and CAn (m_1) unit to EB (m_2) unit, estimated by ^{13}C CP-MAS NMR. ^e Molar ratio of IAn unit to CAn unit, estimated by ^{13}C CP-MAS NMR. ^f Degree of cross-linking, estimated by ^{13}C CP-MAS NMR.

Table IV. Thermal properties of poly(IAn-co-EB) (1), poly(CAn-co-EB) (2), and cross-linked poly(IAn-co-EB)

Sample	m_1/m_2^a	IAn/CAn ^b	Z ^c	$M_n^d \times 10^{-4}$	M_w/M_n^d	T_g^e	T_m^e	ΔH^e
	mol%	mol%	Mol%			°C	°C	
Poly(IAn-co-EB) (1)	36/64	52/48	28	0.27	1.9	-9	119	9.6
	41/59	47/53	27	0.31	1.8	-9	125	5.6
	46/54	60/40	29	0.47	6.3	7	— ^f	— ^f
	49/51	42/58	19	0.33	3.3	11	164	2.6
	49/51	53/47	29	0.87	7.7	10	— ^f	— ^f
Poly(CAn-co-EB) (2)	33/67	100/0	0	0.24	1.9	-2	121	9.6
	36/64	100/0	0	0.43	1.8	-3	120	5.6
	43/57	100/0	0	0.22	1.7	-3	128	3.4
	50/50	100/0	0	0.23	1.7	1	164	2.6
	50/50	100/0	0	0.40	1.8	4	164	2.6
Poly(EB) homopolymer				5.0	1.8	-124	-52	22.2
Cross-linked poly(IAn-co-EB)	31/69 ^g	84/16 ^g	62 ^g			14	— ^f	— ^f
Cross-linked poly(IAn-co-EB)	45/55 ^g	77/23 ^g	59 ^g			18	— ^f	— ^f

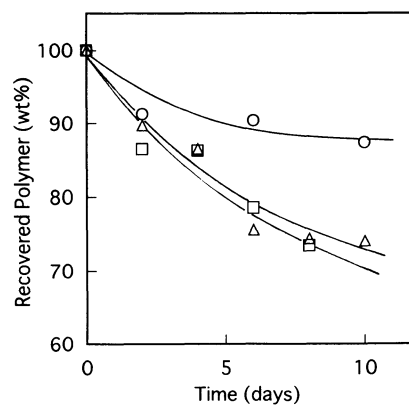
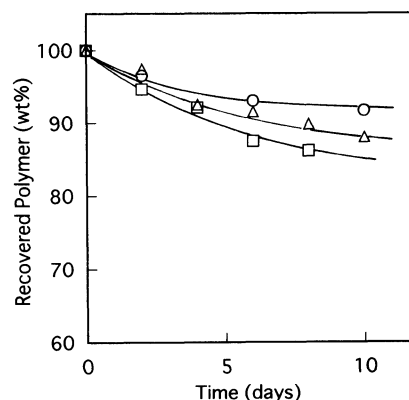
^a Molar ratio of IAn or CAn (m_1) unit to EB (m_2) unit in polymer, by ¹H NMR in CDCl₃. ^b Molar ratio of IAn to CAn unit in polymer, by ¹H NMR in CDCl₃. ^c By ¹H NMR in CDCl₃. ^d By SEC in THF (polystyrene standards). ^e By DSC (heating rate: 10°C min⁻¹). ^f Not detected. ^g Estimated by ¹³C CP-MAS.


Figure 3. ¹³C CP-MAS NMR spectrum of cross-linked poly(IAn-co-EB) synthesized using Mg(OEt)₂.

by the presence of cross-links produced through the cleavage of exo-type double bond in IAn unit.

Enzymatic Degradation

On the enzymatic degradation of the cross-linked copolyesterether and polyester films at 37°C, the recovery of the sample films is depicted in Figures 4 and 5. The enzymatic degradation tests of the copolymer 1 could not be performed because the film prepared by casting from CHCl₃ solution was brittle owing to the relatively low molecular weight. In comparison with the spontaneous hydrolysis in the phosphate buffer solution, the sample films in the phosphate buffer in the presence of *Pseudomonas* sp. and *Rhizopus delemar* (Figures 4 and 5) lipase degraded more rapidly. Recovery of the cross-linked copolyesterether film after 8 days tests by *Pseudomonas* sp. and *Rhizopus delemar* lipase was


Figure 4. Changes of the weight of cross-linked poly(IAn-co-EB) (copolyesterether) film in enzymatic degradation: ○, blank test; □, *Pseudomonas* sp. lipase; △, *Rhizopus delemar* lipase (37°C, pH 7.0).

Figure 5. Changes of the weight of cross-linked poly(IAn-co-EB) (polyester) film in enzymatic degradation: ○, blank test; □, *Pseudomonas* sp. lipase; △, *Rhizopus delemar* lipase (37°C, pH 7.0).

73.5 wt% and 74.4 wt%, respectively, whereas for cross-linked polyester films, 86.2 wt% and 89.8 wt%. The results reveal that the enzymatic degradation rate for the cross-linked copolyesterether film is higher than that of the cross-linked polyester film, which may be interpreted

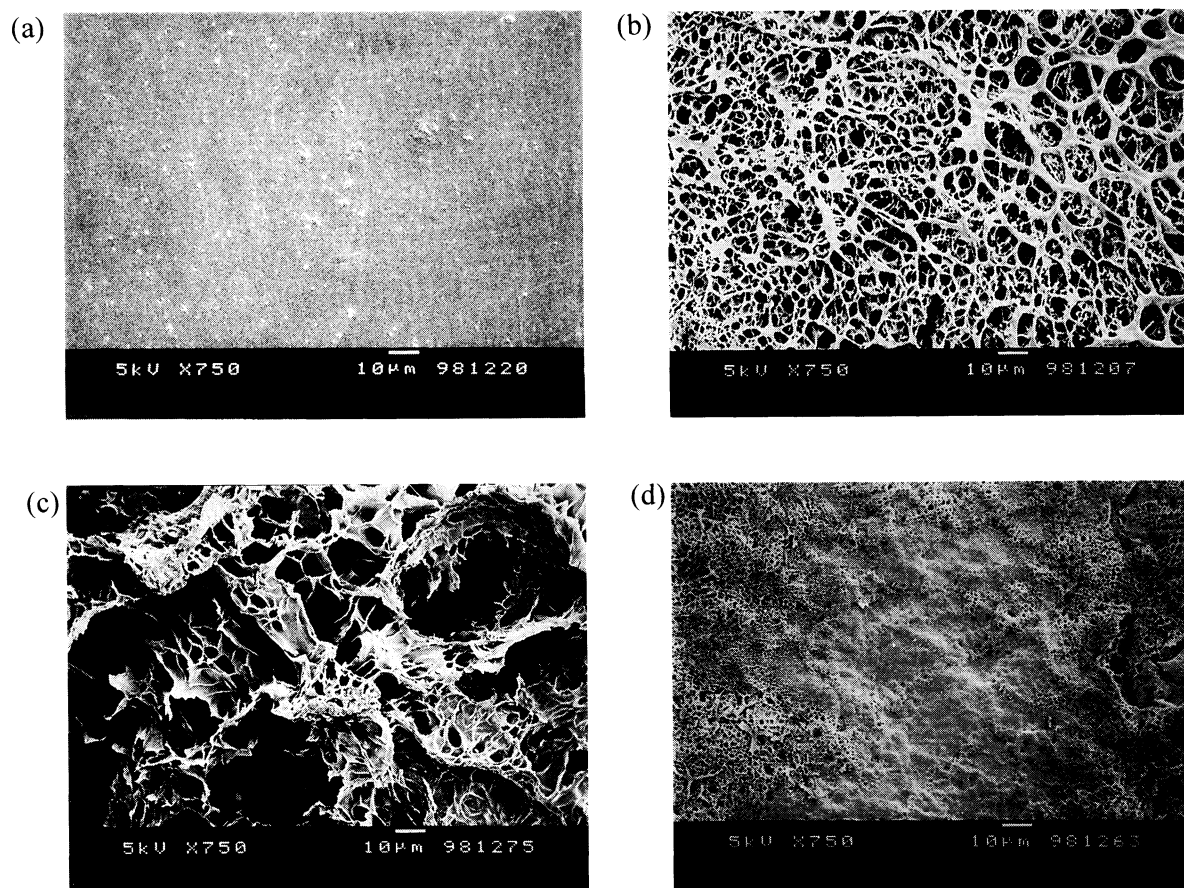


Figure 6. SEM photographs of the surfaces of cross-linked poly(IAn-co-EB) (copolyesterether) film after enzymatic degradation (37°C, pH 7.0): (a), before degradation test; (b), after 10 days degradation test by *Pseudomonas* sp. lipase; (c), after 10 days degradation test by *Rhizopus delemar* lipase; (d), after 10 days blank test.

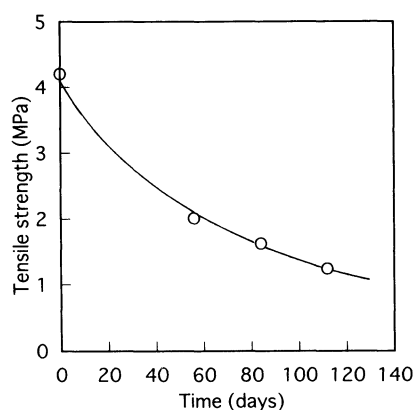


Figure 7. Changes of tensile strength of cross-linked poly(IAn-co-EB) (copolyesterether) film in the soil burial test.

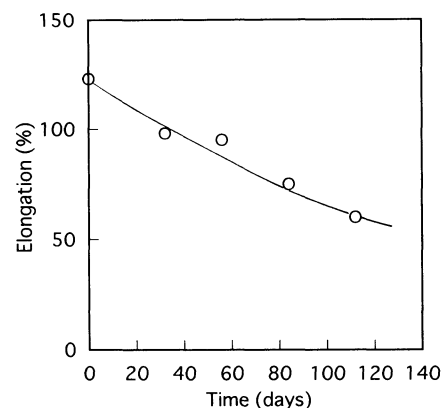


Figure 8. Changes of elongation at break of cross-linked poly(IAn-co-EB) (copolyesterether) film in the soil burial test.

in terms of the flexibility of the networks, *i.e.*, increase of EB homosequence, which must act as a flexible spacer, favors the accessibility of the enzyme to the ester linkage in the network to be cleaved. The more flexible molecular motion of cross-linked copolyesterether film than that of the cross-linked polyester film has been already pointed out in T_g measurement by DSC (see Table IV).

Enzymatic degradation was monitored by SEM observation. Figure 6 shows SEM photographs of the surfaces of the cross-linked copolyesterether film before and after degradation. On the surfaces of the film after 10 days, numerous holes (diameter: 10–40 μm) (Figures

6b and 6c) were observed. Although round holes (2–5 μm) were also observed on the surface after 10 days blank test determined by the experiments in the absence of the lipases (Figure 6d), the surfaces in the enzymatic tests were eroded away more remarkably. These results indicate the sample films are potentially biodegradable.

Soil Burial Degradation (Field Test)

Soil burial degradation was tested on cross-linked copolyesterether film (30 \times 5 \times 0.5 mm), which was the same film used in the enzymatic degradation test. The samples were placed in a field of Mikawa Textile Research

Institute in Gamogori city. The degraded sample was dug up after the test, and the changes of appearance, mechanical properties, and weight loss were investigated. Although the weight loss of the film after soil burial for 120 days could be hardly observed, the relatively large decrease in mechanical properties was confirmed after the soil burial. Figures 7 and 8 represent the changes of tensile strength and elongation at break in the soil burial test, respectively. Remarkable decrease in tensile strength as well as elongation at the early stage of soil burial tests suggest that random main chain scission of the cross-linked poly(IAn-co-EB) occurs on the film surface. In fact, numerous spores were observed on the film surface in SEM measurement, which were not observed on the original film. From these results it seems that the itaconic acid-based network film is degraded from surface slowly in the soil.

CONCLUSIONS

By ^1H , ^{13}C NMR, and FT-IR analyses of the copolymers ($M_n=0.1\text{--}0.9\times 10^4$) obtained from IAn or CAn and EB by $\text{Mg}(\text{OEt})_2$ initiator, these were found to be alternating copolymers, *i.e.*, polyester containing double bonds in the main or side chain. One-pot preparation of cross-linked copolymers was possible through the cleavage of exo-type double bond of IAn unit in the initial polymers by heating at 120°C , which were readily hydrolyzed with *Pseudomonas* sp. and *Rhizopus delemar* lipase in the water buffered at pH 7.0. On soil burial test of the cross-linked poly(IAn-co-EB) film, moderate degradation was confirmed on the surface.

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