Synthesis and Characterization of Copoly(succinic anhydride-ethylene oxide) -Poly(L-lactide) Block Copolymer

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ABSTRACT : The polymerization of L-lactide (LA) was carried out in the presence of tin (II) 2-ethylhexanoate, Sn-$(Oct)_2$ and copoly[succinic anhydride (SA)-ethylene oxide (EO)] which has a hydroxyl end group. The synthesized copolymers were characterized by GPC, ^{1}H NMR, ^{13}C NMR, and DSC. The products were block copolymers consisting of copoly-(SA-EO) and poly(L-lactide) (PLA) segments. Optical micrographs of the copolymer films confirmed the presence of spherulitic morphology. Spherulite size was enhanced with increase in the LA content in the copolymers. The block copolymers were hydrolyzed with or without lipase and biodegraded by enzymes from microorganisms in activated sludge. Hydrolyzability decreased with increase in LA content in the block copolymers. The solubility of the block copolymers containing LA segment in tetrahydrofuran (THF) was higher than that of copoly(SA-EO).
KEY WORDS Poly(L-lactide) / Synthesis / Block Polymer / Biodegradable /

Biodegradable polymers are promising materials for alleviating plastic industrial and household waste.

Several biodegradable polymers such as poly(ε-caprolactone) (PCL),[1] poly(butylene succinate) (PBS),[2] and polylactides (or polylactic acids),[3-9] produced through organic synthesis, have already been on the market or are on the point of being commercialized. Recently, poly(L-lactide)(PLA) has become a major research subject for many groups of researchers because of its satisfactory degradability, its high tensile strength and a high melting point (above 170℃) compared to other aliphatic polyesters such as PCL and PBS. The monomer and degradation products are not toxic for many vital functions. These properties are suitable not only for biomedical applications, e.g., as materials for controlled release of drugs and sutures,[10-13] but also for every day necessaries. However, to improve properties such as impact strength, biodegradability and hydrophilicity, block copolymers containing PLA segment have been studied.

Block copolymers may serve as emulsifiers for the blends of biodegradable homopolymers. Therefore, the study of such copolymers is of great interest. Diblock copolymers can be used to decrease the size of the blend component domains, and interfacial tension and improve the mechanical properties of immiscible polymer blends. Polyethers,[14-22] PCL,[23-30] and poly(hydroxybutylate) (PHB)[31] having hydroxyl end group have been block copolymerized with PLA. Block copolymers are produced by a polymerization of LA in the presence of one of the above polymers using Sn(Oct)$_2$ or triethyl aluminum as catalyst. A transesterification between two different polymers may result in a new block copolymer.[22,23] Gross et al.[18] reported the production of poly-(PLA-*block*-polyethylene oxide) under random polymerization conditions.

We reported the polycodensation of polyether and copoly[succinic anhydride (SA)-ethylene oxide (EO)] to prepare a biodegradable block copolyesterether and study the relationship between the biodegradability or thermal properties and length of polymer segments.[32-35] Polycondensation between copoly(SA-EO) and polypropylene glycol or triblock (polyethylene oxide–polypropylene glycol– polyethylene oxide) really improved elongation while retaining the biodegradability of copoly(SA-EO).[35] However, the tensile strength was lower than that of low density polyethylene (LDPE) and the melting point was below 100℃. One expected method for improving the mechanical and thermal properties of the copolymer is to introduce the PLA segment into the copoly(SA-EO) segment.

To the best of our knowledge, there have been no reports on a block copolymer consisting of a polyester having succinic acid or SA and PLA except for the polymer composed of D,L-lactide and fumaric acid.[36] In this study, LA was polymerized in the presence of copoly(SA-EO) having an end-hydroxyl group and Sn(Oct)$_2$. Poly[copoly-(SA-EO)-*block*-PLA] obtained were characterized using GPC, ^{1}H NMR, ^{13}C NMR, and DSC. The hydrolyzability was evaluated with or without lipase and effects of the segment length in the block copolymer on their hydrolyzability, and thermal properties were studied.

EXPERIMENTAL

Materials

SA (from Wako Pure Chemical Co. Japan) was recrys-

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tallized from chloroform, (CHCl₃). EO (from Sumitomo Seika Co. Japan) was purified with a trap to trap method on calcium hydride under reduced pressure. LA and D,L-lactide were purchased from Purac Biochem BV, Gorinchem. Magnesium diethoxide, [Mg(OEt)₂], triethyl aluminum (AlEt₃), Sn(Oct)₂ (from Wako Pure Chemical Co. Japan) were used as received. The enzyme for biodegradation was a lipase from *Rhizopus arrhizus* (Boehringer Mannheim). Standard activated sludge was provided from Chemical Inspection & Testing Institute, Japan. A series of copoly(SA-EO)s ($M_n = 2600$—13000) were prepared by a ring-opening copolymerization using Mg(OEt)₂ described in our previous paper.[32] The NMR assignment of the copolymers is as follows. ¹H NMR δ (ppm): 2.67 (s, 4H, -*SA*-), 3.65 (s, 4H, -EO-*EO*-EO-), 3.69 (t, 2H, -SA-*EO*-EO- or -EO-*EO*-SA-), 4.25 (t, 2H, -SA-*EO*-EO- or -EO-*EO*-SA-), 4.30 (s, 4H, -SA-*EO*-SA-), 1.27 (t, 3H, -COOCH₂C*H₃*), 3.82 (t, 2H, -COOCH₂-C*H₂*OH), 4.16 (q, 2H, -COOC*H₂*CH₃) ¹³C NMR (CDCl₃), δ(ppm): 28.90 (-SA-, -CH₂-), 172.00 [-SA-, -O*C*(=O)-], 70.50 (-EO-*EO*-EO-, -CH₂-), 68.99 [-SA-*EO*-EO-, -COOCH₂CH₂O- or -EO-*EO*-SA-, -OCH₂CH₂OC(=O)-], 63.74 [-SA-*EO*-EO-, -COOCH₂CH₂O- or -EO-*EO*-SA-, -OCH₂CH₂OC(=O)-], 62.37 (-SA-*EO*-SA-, -CH₂-), 60.72 (-COOCH₂CH₂OH), 66.35 (-COOCH₂CH₂-OH), 14.17 (-COOCH₂CH₃), 60.75 (-COOCH₂CH₃) However, ¹³C NMR signals of ethoxy end group were not detectable when the M_n of these copolymers were more than 4200.

## Synthesis of Copoly(SA-EO)-PLA Block Copolymer(Scheme)

Copoly(SA-EO) (1 g), LA and Sn(Oct)₂ (0.01 g) were put into an ampule. The feed weight ratio, LA/copoly-(SA-EO) (w/w) was 0.5 to 2.7. The polymerization temperature ranged from 110 (19 h) to 170℃ (2.5 h). The polymerization products were dissolved in CHCl₃ and insoluble materials were removed by filtration. The CHCl₃ solution was concentrated *in vacuo* and the polymers were precipitated with petroleum ether and dried under vacuum at 80℃ for 24 h.

To clarify the mechanism of the LA polymerization in the presence of copoly(SA-EO) and Sn(Oct)₂, LA polymerization without Sn(Oct)₂ was carried out. Copoly(SA-EO) and Sn(Oct)₂ were reacted without LA under the same conditions above described. For comparison, PLA, poly(D,L-lactide), and terpoly(SA-EO-LA) were synthesized under similar conditions.

Blends of PLA and copoly(SA-EO) (feed weight ratio of PLA/copoly(SA-EO); 75/25 and 50/50) were prepared as follows: Both polymers were dissolved in CHCl₃, and reprecipitated by petroleum ether. The polymer blend was dried under vacuum at 80℃ for 24 h.

Preparation of Films

Film specimens (thickness: 50—100 μm) were prepared by compression molding of polymer powder or flake using a laboratory press (G-12, Techno Supply Co., Ltd., Japan) at 5℃ higher than the melting temperature of the copolymers for 30 s at 50 kg cm⁻². The prepared films were aged for 1 h at 100℃ to reach equilibrium crystallinity.
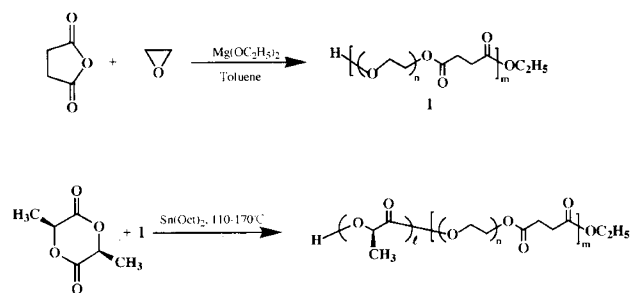
Scheme.

Hydrolysis with Enzyme and without Enzyme

Enzymatic hydrolysis was carried out as follows: Twenty five mg of polymer samples (powder or flake and film) and 2 mL of phosphate buffer (KH₂PO₄/Na₂HPO₄, pH 7.0) were placed in a test tube, and prescribed units of enzyme were added. Blank tests were conducted for the polymers suspended without enzyme and for the enzyme itself. The enzyme used was a lipase from *Rhizopus arrhizus*. Enzymatic hydrolysis was carried out at 37℃ for a fixed time. After filtration (0.2 μm membrane filter), total organic carbon (TOC) of the filtrate was measured with a TOC analyzer (Shimadzu TOC 500). Net TOC were calculated by subtracting the average values at the two control tests from the average of two measurements.

Hydrolysis without enzyme was performed at 70℃ in distilled water for 5 days and the control test was carried out at 30℃ under the same conditions. TOC measurements were carried out by the same method as hydrolysis with enzyme.

Degradation by Activated Sludge

A schematic diagram of the apparatus for an aerobic degradation was described in detail elsewhere.[37] The supernatant (30 mL, MLSS, 30 mg) of standard activated sludge and a polymer film sample (0.2 g) were placed in a fermenter containing a carbon-free culture medium (500 mL, pH 7.0) according to ASTM D 5209-92. The fermenter was incubated at 30℃, aerated with CO₂- free air under magnetic stirring. The evolved CO₂ was absorbed into a 0.5% sodium hydroxide solution and determined by inorganic carbon concentration (IC) measurement for the alkaline solution with a TOC analyzer at every definite time until the evolution rate reached a plateau. Biodegradation (%) of polymers was calculated from the following equation:

$$\text{Biodegradation (\%)} = \frac{\text{Experimentally measured } CO_2}{\text{Theoretical } CO_2} \times 100$$

Theoretically released CO₂ was calculated from the chemical structural formula of these copolymers, assuming that oligomers or monomers, initially formed by enzymatic hydrolysis were completely mineralized to CO₂.

Analytical Procedures

Characterization of Copolymers. ¹H and ¹³C NMR spectra were recorded on a Varian UNITYplus-400 spectrometer (400 MHz and 100.57 MHz, respectively). All spectra were obtained from chloroform-*d* solutions at room temperature with tetramethylsilane (TMS) as the

Table I. Copolymerization results of L-lactide with copoly(SA-EO) [a]

Run	Lactide (L/D)	Copoly(SA-EO) Comp.[SA]/[EO] (molar ratio)	M_n ($\times 10^{-3}$)	Feed ratio LA/Copoly(SA-EO) (w/w)	Catalyst	Temp. °C	Time h	Yield %	[L]/[Copoly(SA-EO)] [b] (molar ratio)	[SA]/[EO] [c] (molar ratio)	M_n [d] ($\times 10^{-3}$)	M_w/M_n [d]
1	L-	48/52	6.3	73/27	Sn(Oct)$_2$	110	19	84	69/31	42/53	12.3	2.8
2	L-	48/52	6.3	67/33	Sn(Oct)$_2$	110	19	96	56/44	44/56	11.0	2.7
3	L-	48/52	4.2	50/50	Sn(Oct)$_2$	110	19	76	40/60	45/55	5.2	2.4
4	L-	48/52	6.3	20/80	Sn(Oct)$_2$	110	19	82	12/88	47/53	5.6	2.7
5	L-	47/53	6.7	73/27	Sn(Oct)$_2$	145	5	87	62/38	44/56	19.4	2.1
6	L-	47/53	6.7	67/33	Sn(Oct)$_2$	145	5	80	54/46	45/55	11.6	2.1
7	L-	47/53	6.7	50/50	Sn(Oct)$_2$	145	5	86	35/65	46/54	8.1	2.1
8	L-	47/53	6.7	73/27	Sn(Oct)$_2$	170	2.5	86	55/45	46/54	12.0	1.9
9	L-	47/53	6.7	67/33	Sn(Oct)$_2$	170	2.5	84	58/42	47/53	9.9	1.9
10	L-	47/53	6.7	50/50	Sn(Oct)$_2$	170	2.5	80	33/67	44/56	7.3	1.9
11	D,L-	48/52	6.3	73/27	Sn(Oct)$_2$	110	19	79	61/39	44/56	13.7	2.5
12	L-	48/52	6.3	73/27	AlEt$_3$	110	19	55	47/53	47/53	7.8	3.6
13	None	48/52	6.3	0/100	Sn(Oct)$_2$	145	5	98	0/100	48/52	5.4	1.9
14	L-	48/52	6.3	67/33	None	145	5	—	0/100	48/52	6.4	1.9
15	L-	—	—	100/0	Sn(Oct)$_2$	110	19	90	100/0	—	22.0	3.3

[a] Polymerization was carried out using copoly(SA-EO) (1 g) and Sn(Oct)$_2$ (0.01 g) as a catalyst. [b] Determined by ^{1}H NMR. [L] shows L-lactic acid unit (a half of LA unit). [c] Compositions of copoly(SA-EO) segments in block copolymers. [d] Determined by GPC measurement (solvent : CHCl$_3$, standard : polystyrene).

internal standard. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrometer, using film samples cast on a potassium bromide plate from CHCl$_3$ solutions. Differential scanning calorimetry (DSC) measurements were made with a Seiko Denshi DSC120. The DSC samples varied from 4 to 8 mg , and the heating rate was 10 °C min^{-1} in the range of temperature from -70 to 120°C (first scan). After the first run, the sample was cooled to -80°C at a rate of *ca.* 10°C min^{-1}, followed by second run under the same conditions. Molecular weight (M_n) and weight distributions (M_w/M_n) were determined with GPC (TOSOH, HCL-8020). The columns were a TSKgel G4000HXL and a TSKgel G3000HXL with limited exclusion molecular weight of 4×10^5. CHCl$_3$ was used as eluent at a flow rate of 0.6 mL min^{-1}. Polystyrene standards with low polydispersity were used to generate a calibration curve. The morphology of each sample was investigated using a Olympus polarizing microscope (Model B 071). Solubility of the copolymers in THF or THF/CHCl$_3$ was examined at room temperature or 40°C.

RESULTS AND DISCUSSION

Polymerization of Lactide

LA was polymerized in the presence of Sn(Oct)$_2$ and copoly(SA-EO). The results are summarized in Table I. The feed weight ratios, LA/copoly(SA-EO), were varied at 0.25—2.7. The compositions, [L], [SA], and [EO] in the block copolymers were determined by ^{1}H NMR analysis. [L] shows L-lactic acid unit which is a half of LA monomer unit in the copolymers. The polymerization yields using Sn(Oct)$_2$ as a catalyst were higher than 80%. Table I shows that the composition, [L]/[copoly(SA-EO)], of the obtained copolymers changed with the feed weight ratio of LA monomer and copoly(SA-EO). When the LA monomer in feed was rich, [L] of the copolymers proportionally increased with LA weight ratio in feed and M_ns were over 10000 (Run 1, 2 in Table I). There was a similar tendency with change in temperature and the higher temperature shortened the polymerization time. Using

AlEt$_3$ as a catalyst instead of Sn(Oct)$_2$, the polymerization yield was rather low (55%) and in the absence of catalyst, LA polymerization did not proceed completely (Run 12, 14). The composition, [EO] in the block copolymers was slightly rich compared with that of the original copoly(SA-EO). This suggests that the copoly(SA-EO) as a prepolymer might decompose through LA polymerization. A small amount of succinic anhydride residue was observed in the reaction flask at the end of copolymerization in many cases. The [SA]/[EO] ratios were the same as those of the original copoly(SA-EO) in the absence of LA monomer (Run 13) or Sn(Oct)$_2$ (Run 14). Therefore, the decomposition of copoly(SA-EO) seems attributable to LA monomer and Sn(Oct)$_2$, although, the decomposition mechanism of the copoly(SA-EO) is not still clear.

The typical GPC curves of synthesized copolymers are shown in Figure 1. All GPC curves showed unimodal. As LA weight ratio in feed monomers increased, the peak in the GPC curves shifted to higher molecular weight zone. In the case of low weight ratio of LA (**a**, Run 4 in Table I), the GPC curve was situated in the lower molecular weight zone than that of copoly(SA-EO), (**b**), supporting that the copoly(SA-EO) is partially decomposed through LA polymerization.

The molecular weights of the block copolymers and copoly(SA-EO)s as prepolymer are summarized in Table II. $M_{n\,\text{calc.}}$ stands for the M_n calculated on the basis of feed weight of LA monomer and polymerization yield. $M_{n\,\text{calc.}}$ was higher than that determined by GPC measurement ($M_{n\,\text{gpc}}$). The difference between the $M_{n\,\text{calc.}}$ and the $M_{n\,\text{gpc}}$ of copolymer seems to be caused not only by the imperfect initiation of LA monomer, but by the decomposition of copoly(SA-EO) through the LA copolymerization. $M_{n\,\text{PLA}}$s which represent M_n of PLA segment in block copolymer were calculated from the intensity ratio between $-$OCH(CH_3)CO$-$ and HOCH(CH_3)CO$-$ in ^{1}H NMR spectra. In many cases (Run 1, 2, 6, 8, 9, 11 and 12 in Table II), $M_{n\,\text{PLA}}$s were found to be almost half the increase of ΔM_n ($\Delta M_n = M_{n\,\text{gpc}} - M_{n0}$) ($M_{n0}$ means $M_{n\,\text{gpc}}$ of the
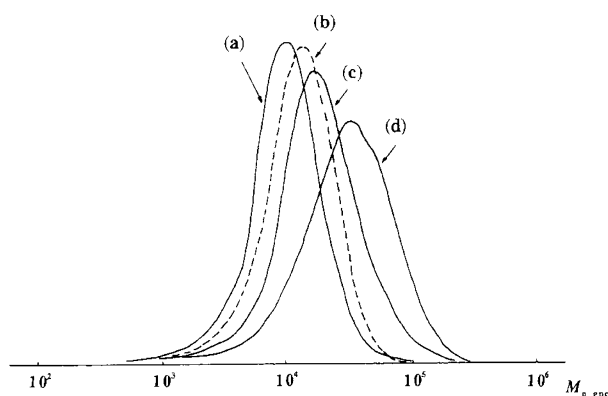
Figure 1. GPC profiles of typical copolymers : (a) ; Polymerized at feed weight ratio, LA/copoly(SA-EO)=0.25 for 19 h at 110℃ (Run 4 in Table I), (b) ; Copoly(SA-EO) (M_n=6700, M_w/M_n=2.0) used as prepolymer in the LA polymerization, (c) ; Polymerized at feed weight ratio, LA/copoly(SA-EO)=2.0 for 5 h at 145℃(Run 6), (d) ; Polymerized at feed weight ratio, LA/copoly(SA-EO)=2.7 for 5 h at 145℃(Run 5).

Table II. Molecular weights (M_n) of block copolymers and copoly(SA-EO)s as a prepolymer

Run	$M_n(\times 10^{-3})$				
	$M_{n\ \text{calc.}}$[a]	$M_{n\ \text{gpc}}$[b]	$M_{n\ \text{PLA}}$[c]	M_{n0}[d]	ΔM_n[e]
1	20.6	12.3	3.2	6.3	6.0
2	18.4	11.0	2.0	6.3	4.7
3	7.4	5.2	2.5	4.2	1.0
4	8.1	5.6	0.55	6.3	−0.7
5	22.4	19.4	2.3	6.7	12.7
6	17.4	11.6	2.0	6.7	4.9
7	12.5	8.1	1.4	6.7	1.4
8	22.3	12.0	2.4	6.7	5.3
9	18.0	9.9	2.6	6.7	3.2
10	12.1	7.3	1.0	6.7	0.6
11	19.7	13.7	2.5	6.3	7.4
12	11.0	7.8	1.9	6.3	4.7
13	—	5.4	—	6.3	−0.9
14	—	6.4	—	6.3	0.1
15	—	22.0	—	—	22.0

[a] Expected number-average molecular weight calculated from yield and monomer/hydroxyl group ratio. [b] Determined by GPC measurement. [c] M_n of PLA segment in block copolymer based on the integration strength ratio,-CH(CH_3)CO-/HOCH(CH_3)CO- in ^{1}H NMR spectra. [d] M_n of copoly(SA-EO) as a prepolymer. [e] $\Delta M_n = M_{n\ \text{gpc}} - M_{n0}$.

original copoly(SA-EO) used as prepolymer.) In Runs 3, 4, 7, and 10, $M_{n\ \text{PLA}}$s were not agreement with ΔM_ns. These results suggest that the obtained copolymers were ABA type (A ; PLA, B ; copoly(SA-EO)) when the feed ratio of LA monomer is rich, and that the obtained copolymers were AB or ABA with a slight decomposition when the LA feed ratio is low.

M_w/M_ns of the copolymers synthesized at 110℃ were higher than those of the block copolymers synthesized at 145℃ or 170℃. T_ms of the block copolymers are higher than the polymerization temperature, 110℃ as described below. The copolymers are in a solid state during increase in M_n of PLA segment. T_m of copoly(SA-EO) is lower than 110℃. Consequently, the LA polymerization system at 110℃ changes from homogeneous to heterogeneous with LA polymerization.

Figure 2 shows ^{1}H NMR and ^{13}C NMR spectra for the relatively low M_n of copolymer (M_n=5200, Run 3 in Table I). ^{1}H NMR and ^{13}C NMR analyses of PLA[39] and block copolymer containing PLA block , e.g., poly(ethylene glycol) (PEG)-PLA di- or triblock copolymer,[14,17—20] PCL-PLA block copolymer,[25, 26] PHB-PLA diblock copolymer[31] have been reported. The assignments of ^{1}H NMR and ^{13}C NMR spectra in Figure 2 were conducted based on literature data together with copoly(SA-EO) (see EXPERIMENTAL Section). ^{1}H NMR spectrum shows signals derived from copoly(SA-EO) segment except for the signals of -COOCH_2CH$_3$ (i in Figure 2) and -COOCH$_2$CH_2OH. Moreover, from PLA segment, the signals were detected such as -CH_3, d., δ 1.58 ppm, J = 6.8 Hz, -CH(CH$_3$)-, q., δ 5.16 ppm, J =7.1 Hz, and -SA-EO-LA-, -CH_3, d., δ 1.52 ppm, J =7.2 Hz, -CH(CH$_3$)-, d., δ 5.1—5.2 ppm, J =7.2 Hz, and from end groups of copolymer such as HOCH(CH$_3$)CO-, q., δ 4.3—4.4 ppm and HOCH(CH_3)CO-, d., δ 1.49 ppm, J =7.2 Hz.

The ^{13}C NMR spectrum shows signals derived from copoly(SA-EO) segment such as -SA-, -CH$_2$-, δ 28.80 ppm, -OC(=O)-, δ 171.99 ppm, -SA-EO-SA-, -CH$_2$-, δ 62.35 ppm, from PLA segment such as -CH$_3$, δ 16.62 ppm, -CH(CH$_3$)-, δ 69.99 ppm, -OC(=O)-, δ 169.57 ppm, from end group of copolymer, HOCH(CH$_3$)CO-, δ 66.69 ppm, HOCH(CH_3)CO-, δ 20.49 ppm, and -CH-

(CH$_3$)COOCH$_2$CH$_2$O-, δ 63.71 ppm. The last signal indicates the existence of EO-LA bonds in the copolymer. The peak height of HOCH(CH$_3$)CO- was equivalent to that of -CH(CH$_3$)COOCH$_2$CH$_2$O-. The ^{1}H NMR signal of -COOCH$_2$CH_2OH (δ 3.81 ppm, J =6.8 Hz) in copoly(SA-EO) as a prepolymer was not detectable after copolymerization with LA. These results support the obtained copolymer (Run 3 in Table I) is a block copolymer. The terminal-OH group in the copoly(SA-EO) is important in the LA polymerization with Sn(Oct)$_2$. NMR analysis of such a block copolymer having PLA block, for example PLA-PEG-PLA[14,17—20] triblock copolymer, PCL-PLA diblock copolymer,[23,25,26] and PHB-PLA diblock copolymer[31] has been discussed. However, a block copolymer containing succinic acid unit has not been studied.

By NMR end analysis, the ratio of ABA/AB could be calculated. However, in this case, this is difficult because a) ^{1}H NMR methyl and methyne signals of OH end unit [HOCH(CH_3)CO-] overlap with other signals (1.52 and 4.3 ppm), and b) ^{13}C NMR signals of ethyl ester end unit are not quantitatively clarified against noise. At first, we presumed that an AB block copolymer could be obtained in the presence of copoly(SA-EO) having one OH endgroup. However, ABA type block copolymers were synthesized in many cases. This suggests that reactive OH groups at both ends derived from copoly(SA-EO) may be produced by the decomposition of copoly(SA-EO).

The mechanism of LA polymerization in the presence of Sn(Oct)$_2$ and a polymer having OH-end group (or alcohol) as a macroinitiator has been investigated by Kricheldorf et al.[38] and Nijenhuis et al.[39] Their polymerization mechanisms differ in formation of coordination compounds at the initiation step in the LA polymerization. Kricheldorf et al. proposed that the coordination compound between Sn(Oct)$_2$ and OH-end group is formed at first, followed by insertion of LA monomer into the coordination compound. Nijenhuis et al. suggest the formation of the coordination compound between Sn (Oct)$_2$ and LA, followed by reaction of OH-end group and
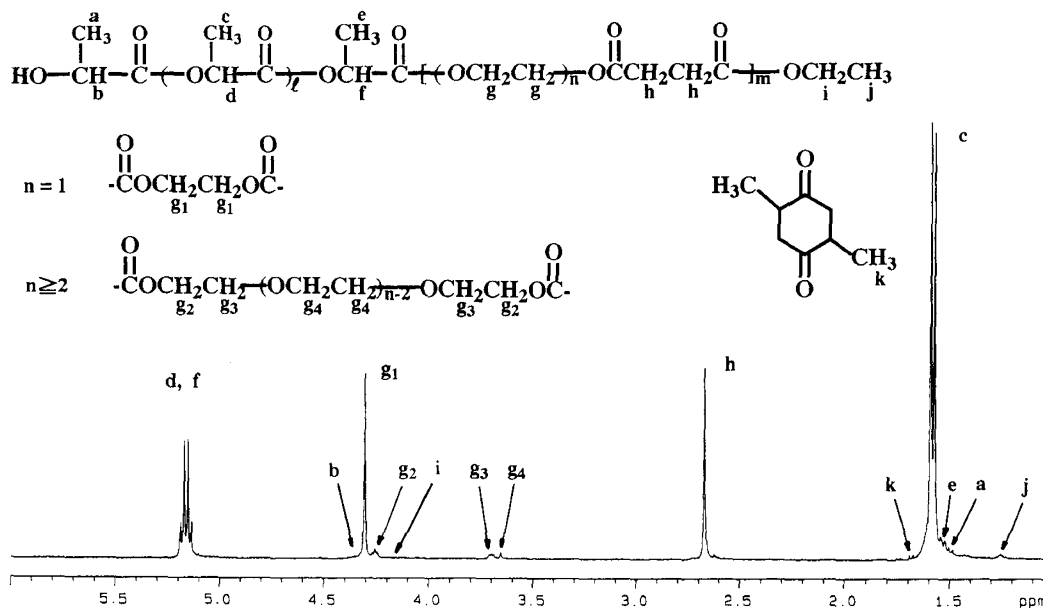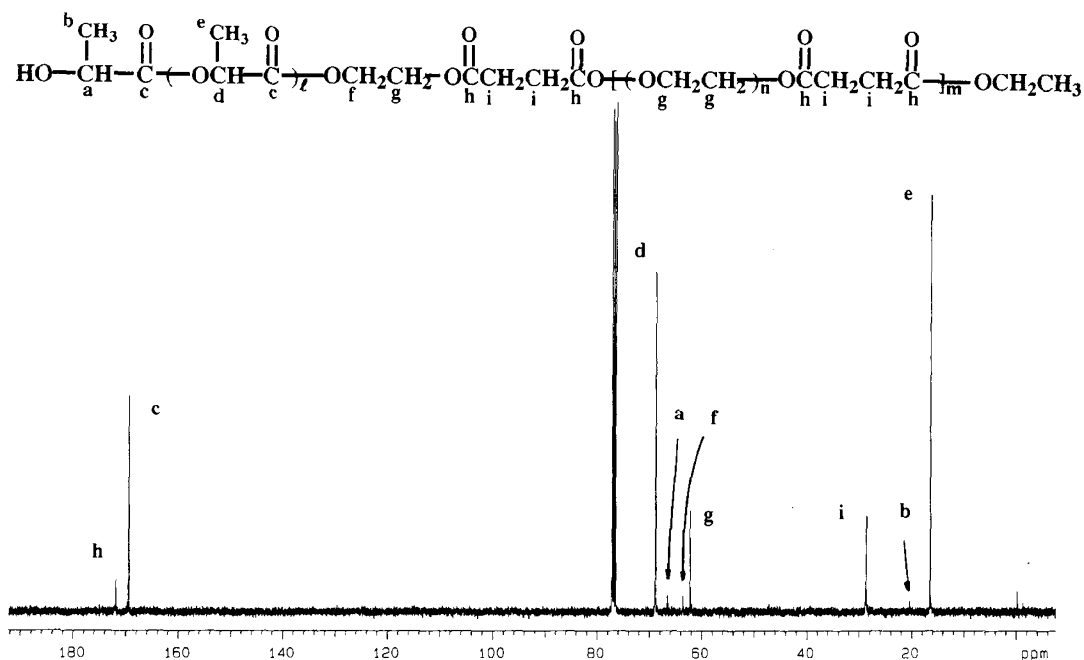
^{1}H NMR

^{13}C NMR

Figure 2. ^{1}H NMR and ^{13}C NMR of copoly(succinic anhydride-ethylene oxide)–poly(L-lactide) block copolymer (Run 3 in Table I) polymerized at feed weight ratio, LA/copoly(SA-EO) = 1 for 19 h at 110℃.

the coordination compound. We tried to clarify the LA initiation mechanisms in the presence of Sn(Oct)$_2$ and copoly(SA-EO) having one OH-end group on the base of the characterization of block copolymers synthesized under various polymerization conditions. However, the conclusion with respect to LA initiation mechanisms was not confirmed by the experimental results. It is necessary to investigate fundamentally the mechanism of the LA polymerization.

Thermal Properties of Copolymers

Melting point (T_m), heat of fusion (ΔH), and glass transition temperature (T_g) of the copolymers obtained were determined by DSC first run. Crystallization temperature (T_c) was obtained from DSC second run. The thermal properties are summarized in Table III. Some representative DSC traces of typical block copolymers are shown in Figure 3.

The DSC first run curve of the copolymer (c in Figure 3, Run 6 in Table I)) synthesized by LA polymerization in the presence of copoly(SA-EO) and Sn(Oct)$_2$ showed

Table III. Thermal properties of block copolymers and homo polymers

Run	Thermal propeties			
	$T_m{}^a$	$\Delta H{}^a$	$T_g{}^b$	$T_c{}^b$
	℃	mJ mg^{-1}	℃	℃
1	172	35	−13, 45	82
2	170	24	−10, 40	78
4	94	36	−9	ND^c
5	167	27	30	83
6	90, 164	3, 22	21	80
7	82, 159	10, 7	6	60,89
8	160	30	29	89
9	154	16	16	100
10	143	14	−4	ND^c
11	84, 89	13, 1	32	ND^c
12	94, 163	32, 5.2	−13, 2	ND^c
Copoly(SA-EO)^d	96	98	−18	32
Poly(L-lactide)^e	181	42	64	111
Poly(D,L-lactide)^f	ND	ND	25	ND^c
Terpoly(SA-EO-LA)^g	79, 85	5, 5	25	ND^c
Blend-1^h	178	26	−19, 57	25, 163
Blend-2^i	95, 178	22, 17	−17, 58	29, 69, 162

^{a} Determined by DSC (first run). ^{b} Determined by DSC (second run). ^{c} Not detected. ^{d} [SA]/[EO] = 47/53, M_n = 6700. ^{e} M_n = 24500, M_w/M_n = 2.9. ^{f} M_n = 22000, M_w/M_n = 3.3. ^{g} M_n = 2500, M_w/M_n = 2.8, [SA]/[EO]/[L] = 15/22/63. ^{h} Feed weight ratio, PLA/ copoly(SA-EO) = 75/25, [SA]/[EO]/[L] = 13/17/70. ^{i} Feed weight ratio, PLA/copoly(SA-EO) = 50/50, [SA]/[EO]/[L] = 28/33/39.
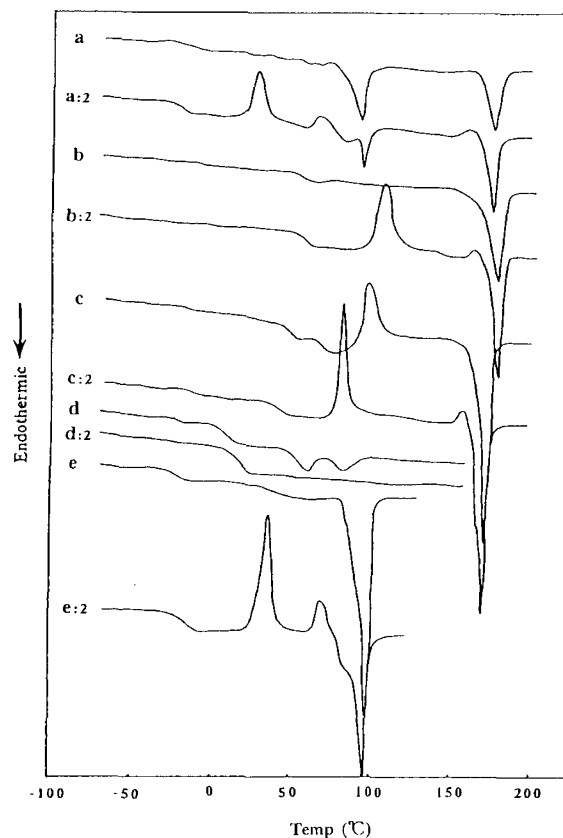

Figure 3. DSC scans of copolymers at a scan rate of 10℃ min^{-1}: (a); blend[copoly(SA-EO)–PLA], (b); PLA (Run 15 in Table I), (c); poly[copoly(SA-EO)-*block*-PLA)] (Run 6 in Table I), (d); terpoly-(SA-EO-LA), (e); copoly(SA-EO) (M_n=6700, M_w/M_n=2.0). 2; DSC *second run*.

two endothermic peaks (at 90℃ and 164℃) derived from crystal fusion of copoly(SA-EO) segment and PLA segment. The endothermic peak derived from copoly(SA-EO) segment was broad and small because of overlapping with the exothermic peak of crystallization of PLA segment. The two T_ms of these copolymers shifted slightly toward lower temperatures because of compatibility of two different segments. ΔH of PLA segment increased with LA feed ratio. The DSC first run of blend copolymer (weight ratio of PLA to copoly(SA-EO)=75/25, a in Figure 3) showed no crystallization peak and had two endothermic peaks derived from crystal fusion of copoly(SA-EO) and PLA segments. T_ms of the blend copolymer were the same as those of feed homopolymers. Although, the DSC curve of the terpoly(SA-EO-LA) (M_n =2500, [SA]/[EO]/[LA]=15/22/63, see EXPERIMENTAL section) had two small endothermic peaks. ^{1}H NMR spectra of the terpolymer showed the signal of LA homo sequence (–CH$_3$, d., δ 1.57 ppm, J=7.2 Hz). These results support the view that the terpolymer containes a short LA sequence.

T_g of the copolymer synthesized by the ring-opening polymerization of LA in the presence of copoly(SA-EO) and Sn(Oct)$_2$ shifted to the temperature of about 10℃ lower than those of PLA and the above blend. T_g of the copolymer from DSC second run shifted to a temperature of about 15℃ lower than that from first run. This was not observed for DSC of PLA and the blend of PLA and copoly(SA-EO).

T_c of the copolymers obtained decreased compared with that of PLA and the blends, suggesting that the rate of crystallization of PLA segment in the copolymer decreases because of block copolymerization.

DSC and GPC measurements and the spectra of ^{1}H NMR and ^{13}C NMR show clearly that the copolymer synthesized by the ring-opening polymerization of LA in

the presence of copoly(SA-EO) with Sn(Oct)$_2$ is a block copolymer containing PLA segment and copoly(SA-EO) segment.

Figure 4 shows the DSC curves of the block copolymers synthesized by polymerization of LA [feed weight ratio of LA/copoly(SA-EO)=2] in the presence of copoly-(SA/EO) and Sn(Oct)$_2$ at various temperatures and times. DSC curves for the block copolymer synthesized at 110℃ for 19 h (Run 2 in Table I) were similar to those of the copolymer synthesized at 145℃ for 5 h (Run 6). The T_m of the block copolymer synthesized at 145℃ for 5 h (Run 9) was higher than that of the copolymer synthesized at 110℃ for 19 h. An increase in M_n of the block copolymer turned out to lead to higher T_m. The endothermic peaks in DSC curves of the block copolymer synthesized at 175℃ for 2.5 h were broad and small and shifted to lower temperatures compared to those of block copolymer synthesized under other two different conditions. A transesterification reaction initiated by a temperature rise resulted in a decrease in the M_n of the block copolymer. These results and the decrease of SA content of copoly(SA-EO) segment in the block copolymer through LA polymerization (Table I) suggest that a transesterification occurred partially during the polymerization of LA. Increase in reaction temperature promoted the transesterification. This agrees with Ikada et al.[40] for the homopolymerization of LA with Sn(Oct)$_2$. However, a transesterification mechanism of the block copolymer in-
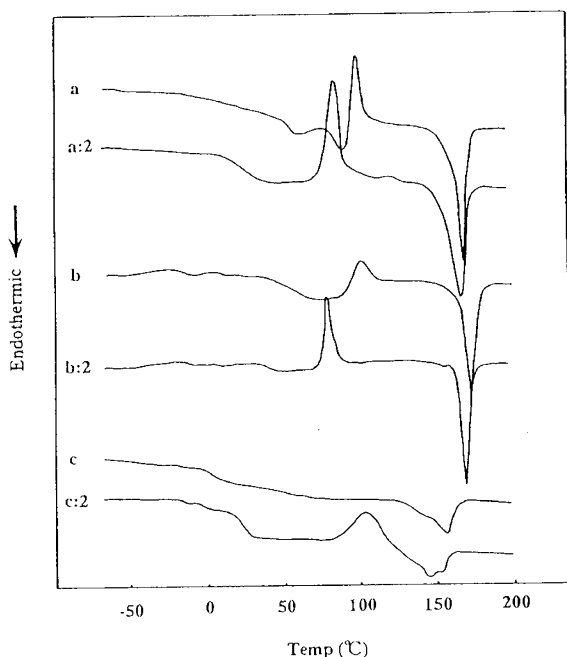
Figure 4. DSC scans of poly[copoly(SA-EO)-*block*-PLA] : (a) ; Polymerized at 110°C for 19 h (Run 2 in Table I), (b) ; polymerized at 145°C for 5 h (Run 6), (c) ; polymerized at 170°C for 2.5 h (Run 3).

cluding copoly(SA-EO) and PLA segment is not clear.

Morphology of Block Copolymers

Optical micrographs of block polymer films with PLA and the blend (Blend 1 in Table III) of PLA and copoly-(SA-EO) are shown in Figure 5. All polymer films after compression molding (see EXPERIMENTAL section) were rapidly cooled to room temperature and crystallized at 100°C for 30 min. PLA (**a**), the block copolymer (**b**, **c**) and chain-extended copoly(SA-EO)[41] (**d**) showed a spherulitic morphology. Tsuji and Ikada[42,43] reported that the growth rate and size of spherulite for the as-cast PLA film crystallized at annealing temperature ranging 60 to 100°C though quick quenching to 0°C after melting the polymer is lower than those for film crystallized at above-mentioned temperature from the melt. The samples studied here were quenched to room temperature from the melt, followed by crystallization at 100°C for 1 h. Spherulites in the block copolymer were smaller than 10 μm because of a faster polymer crystallization. This agrees with Ikada.[41,42] The size of spherulite of the block copolymers increased with LA content in the block co-polymer. In contrast with copolymers (**a**–**c**), the blend (**e**) showed phase separation morphology.

Hydrolysis with and without Lipase

Hydrolysis of these copolymers was carried out with li-pase at 37°C and without lipase at 70°C. The samples of copolymers used for hydrolysis were powder, flakes, dried under vacuum at 80°C for 24 h after precipitation with petroleum ether, or film prepared by compression molding (see EXPERIMENTAL section). The results of hy-drolysis are summarized in Table IV. Enzymatic hy-drolysis of the block copolymer with lipase from *Rhizopus arrhizus* decreased with increase in LA con-tent in the copolymer. Terpoly(SA-EO-LA) containing 63
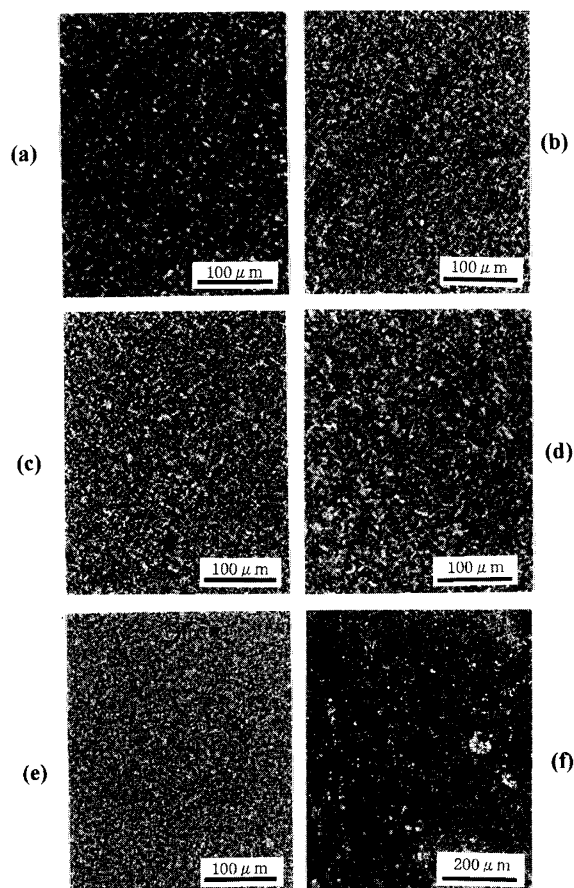

Figure 5. Optical photomicrographs of polymer films crystallized isothermally at 100°C for 30 min after quenching to room tem-perature from the melts : (a) ; PLA, $M_n = 22000$, (b) ; block copoly-mer, $M_n = 8100$, [L]/[copoly(SA-EO)] = 35/65 (Run 7 in Table I), (c) ; block copolymer, $M_n = 11600$, [L]/[copoly(SA-EO)] = 54/46 (Run 6), (d) ; block copolymer, $M_n = 19400$, [L]/[copoly(SA-EO)] = 62/39 (Run 5), (e) ; chain-extended copoly(SA-EO)[41], $M_n = 47500$, [SA]/[EO] = 47/53, (f) ; blend copolymer of copoly(SA-EO) and PLA (weight ratio of PLA/copoly(SA-EO) = 75/25) (Blend-1 in Table III).

molar% of LA was hydrolyzed with lipase because of the short LA length. The hydrolyzability of the block copoly-mer synthesized using $AlEt_3$ as a catalyst (Run 12 in Ta-ble I) was higher than for other block copolymers.

Block copolymers were hydrolyzed without lipase at 70°C. The hydrolyzability of the block copolymer in-creased with decrease in LA content in the copolymer and M_n of PLA segments.

The hydrolyzability of the films was low compared with flake or powder samples. This suggests that the hy-drolysis of the block copolymer occurs mainly at the polymer surface and the latter influences polymer hy-drolyzability.

Biodegradation with Activated Sludge

The relationships of the biodegradation of typical block copolymers *versus* time are shown in Figure 6. The degradability decreased with increase in M_n of PLA seg-ment and LA molar content in the block copolymers. In particular, the block copolymer (Run 7 in Table I) hav-ing long LA was not degraded by activated sludge within the testing period. These results are in agreement with enzymatic hydrolysis by lipase from *Rhizopus arrhizus*.

Table IV. Hydrolyzability of block copolymers and homo polymers with or without lipase

Run	Hydrolyzability, TOC/ppm			
	With lipase [a]		Without lipase [b]	
	Powder or flake [c]	Film [d]	Powder or flake [c]	Film [d]
1	55	—	—	—
2	—	—	910	—
4	—	—	840	—
5	40	30	520	350
6	90	90	740	420
7	220	—	1130	790
11	50	—	—	—
12	350	—	—	—
Copoly(SA-EO) [e]	150	—	340	—
Poly(L-lactide) [f]	2	1	120	40
Poly(D,L-lactide) [g]	1	—	—	—
Terpoly(SA-EO-LA) [h]	670	—	—	—
Blend-1 [i]	25	30	180	170
Blend-2 [j]	80	—	250	—

[a] At 37℃ for 1 day. Lipase (1250U) from *Rhizopus arrhizus* was added. [b] At 70℃ for 5 days. [c] Polymer sample after precipitated with petroleum ether was used. [d] Film was prepared by compression molding. Molding was carried out at a temperature of about 5℃ higher than the melting point of the polymer for 1 min. [e] [SA]/[EO] = 47/53, M_n = 6700. [f] M_n = 24500, M_w/M_n = 2.9. [g] M_n = 22000, M_w/M_n = 3.3. [h] M_n = 2500, M_w/M_n = 2.8, [SA]/[EO]/[L] = 15/22/63. [i] Feed weight ratio, PLA/copoly(SA-EO) = 75/25, [SA]/[EO]/[L] = 13/17/70. [j] Feed weight ratio, PLA/copoly(SA-EO) = 50/50, [SA]/[EO]/[L] = 28/33/39.
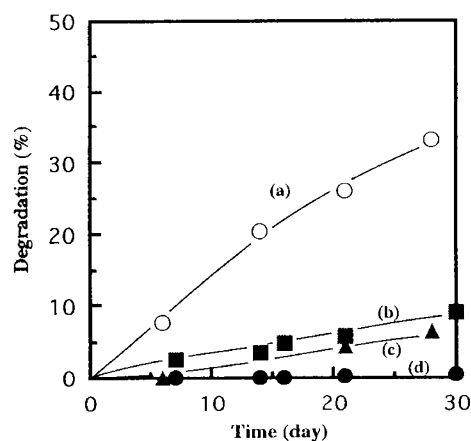

Figure 6. Biodegradation of typical copolymers by standard activated sludge at 30℃ : (a) ; M_n = 7800, [L]/ [copoly(SA-EO)] = 47/53 molar ratio (Run 12 in Table I), (b) ; M_n = 11600, [L]/ [copoly(SA-EO)] = 35/65 molar ratio (Run 6), (c) ; M_n = 12300, [L]/ [copoly(SA-EO)] = 69/31 molar ratio (Run 1), (d) ; M_n = 19400, [L]/ [copoly(SA-EO)] = 62/38 molar ratio (Run 5). The film samples (ca. 50 μ m thick) were prepared by compression molding.

Table V. Solubility of block copolymers in THF or in THF/CHCl₃

Run	Block copolymer		Solubility [a] in THF/CHCl₃ v/v% soln.				Wt% of soluble polymer in THF [c]
	$M_{n \, gpc}$ ($\times 10^{-3}$)	[SA]/[EO]/[L] (molar ratio)	10/90	30/70	50/50	hot THF [b]	
5	19.4	17/21/61	+ +	+ +	+ +	+ +	77
6	11.6	21/25/54	+ +	+ +	+	+ +	80
7	8.1	30/35/35	+ +	+ +	+ +	+ +	68
8	12.0	21/24/55	+ +	+ +	+ +	+ +	87
9	9.9	20/22/58	+ +	+ +	+ +	+ +	89
11	13.7	17/22/61	+ +	+ +	+ +	+ +	88
Copoly(SA-EO)	6.3	48/52/0	+ +	—	—	+	0
Poly(L-lactide)	24.5	0/0/100	+ +	+ +	+	+ +	10
Poly(D,L-lactide)	22.2	0/0/100	+ +	+ +	+ +	+ +	100

[a] + + : Soluble, + : Partially Soluble, — : Insoluble. [b] Temperature 40℃. [c] At room temperature.

TOC of the medium in the incubator filtered by 5A filter paper was measured using a TOC analyzer (see EXPERIMENTAL section) to determine the water-soluble compounds produced after degradation by activated sludge. TOC were below 2 ppm in all cases measured. This indicates that the water-soluble compounds produced by the hydrolysis of block copolymers are rapidly converted into CO_2 and H_2O.

Solubility in THF and in a Different Mixture of THF/CHCl₃

The solubility of the block copolymers and homo polymers in THF and a different mixture of THF/CHCl₃ is given in Table V. All block copolymers and copolymers, except copoly(SA-EO) used as a prepolymer were soluble in hot THF (40℃). The block copolymers and PLA were partially soluble in THF at room temperature. The solubility of block copolymers in THF increased with an increase in LA content in the block copolymers. In comparison with the solubility for Run 7 (or Run 8) and Run

10 (or Run 13), the solubility for the former was greater than that for the latter in spite of equivalent LA content. Small length of copoly(SA-EO) segment in the block copolymer with rise in polymerization temperature (170℃) resulted in greater solubility compared to that of the polymer prepared at low temperature (145℃), considering the DSC results of the block copolymers. Copoly(SA-EO)s having high SA content of 46 to 49 mol% were soluble only in organic chlorinated solvents such as CHCl₃. The block copolymerization of copoly(SA-EO) with PLA brought about higher solubility in THF and in a mixture of THF and CHCl₃.

CONCLUSIONS

The copoly(SA-EO)-PLA block copolymers were synthesized by a ring-opening polymerization of LA in presence of $Sn(Oct)_2$ and copoly(SA-EO) having SA content 47 or 48 mol% and hydroxyl group at one end of the copolymer. M_n of the synthesized block copolymer in-

creased with LA feed weight ratio. Copoly(SA-EO) was slightly decomposed during the LA polymerization. Micrographs of the copolymer films showed spherulitic morphology. Spherulite size became greater with higher LA content in the copolymers. The block copolymers were hydrolyzed with or without lipase and degraded in the presence of enzyme from microorganisms in activated sludge. The hydrolyzability decreased with increase in LA content in the block copolymers. The solubility of the block copolymers containing LA segment in THF was higher than that of copoly(SA-EO). However, the flexibility of PLA could not be improved because of fine crystallinity of copoly(SA-EO) segment having higher SA content. It is expected that PLA may change to soft and biodegradable material by a block polymerization of PLA with copoly(SA-EO) having lower SA content, e.g., 40—42 mol%.

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41. Chain-extension reaction of copoly(SA-EO) was carried out as follows : The copolymer (3 g) was placed in a 100 mL three-necked flask equipped with a stirrer. After the copolymer was molten by heating, titanium tetra-*iso*-propoxide (0.025 g) was added and the mixture was kept stirring under vacuum at 170°C for 4—12 h.
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