Synthesis and Biodegradation of Copolyesterether of Copoly(succinic anhydride/ethylene oxide) with Polyether

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ABSTRACT: The thermal properties and biodegradability of block copolyesterethers based on copoly[succinic anhydride (SA)/ethylene oxide (EO)] (polymer composition range SA/EO 42/58–49/51 mol %), synthesized by ring-opening copolymerization and poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG), were studied. The block copolyesterethers synthesized from higher than 7000 molecular weight (M_n) or high SA content copoly(SA/EO), SA/EO = 48/52 or 49/51, and PEG showed melting points and fusion heats (ΔH) similar to those of the prepolymers without leading to a microphase-separation structure. Enzymatic degradability of the block copolyesterethers synthesized from biodegradable copoly(SA/EO) with a low SA content (SA/EO = 42/58 mol %) and PEG was significantly smaller compared to that of the chain-extended copoly(SA/EO) used as a prepolymer. On the other hand, the block copolymers synthesized by an equimolar amount of copoly(SA/EO) and PPG showed evidence of a microphase-separation structure. An increase in propylene glycol (PG) content interfered with the formation of a microphase-separation structure. However, the block copolyesterethers including nonbiodegradable copoly(SA/EO), with a high SA content (SA/EO = 49/51 mol %), and PPG were found to be enzymatically degradable. In the biodegradation testing with standard activated sludge, the block copolyesterethers were degraded by microorganisms in activated sludge. The relationship between polymer composition and the biodegradation rate by activated sludge shows a similar trend to that of enzymatic hydrolysis. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 2095–2106, 1998

Key words: biodegradation; block copolyesterether; enzyme; activated sludge; differential scanning calorimetry; microphase-separation structure

INTRODUCTION

Polymeric materials have permeated everyday life, in applications primarily on the basis of large-scale production and long-lasting performance. However, people have recently started to realize that the extensive use of "recalcitrant" polymers for short-term applications constitutes a serious burden for the environment.[1] Biodegradable polymers have been put forward as one of the promising approaches toward solving these problems and have been extensively studied by many researchers.[2–25] Biodegradable polymers such as poly(ε-caprolactone),[2,3] polybutylenesuccinate,[4] and polylactides[5–12] have already been on the market or are on the point of being commercialized. There have been many attempts to

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put these polymers into practical use in various fields, making the best of their thermal properties. Many investigations have been undertaken on polylactides,[26–28] such as the polymerization of L-lactide or L-lactic acid, the polymer blends with poly(L-lactide), and the copolymerization of lactides with other monomers.

We have been studying the chain-extension reaction of copoly[succinic anhydride (SA)/ethylene oxide (EO)] synthesized by the ring-opening copolymerization of SA and EO in order to prepare high molecular weight copolyesters or copolyesterethers and previously reported the relationship between the biodegradability and the thermal properties of the copoly(SA/EO)s having different SA molar content and different forms such as powder, bulk flake, and film.[29,30] Furthermore, we have reported that the end groups of these copoly(SA/EO), synthesized by magnesium diethoxide as a catalyst, are the hydroxy group connected with EO and the ethyl ester group connected with SA.[31] In general, modification of a polymer is usually carried out by blending or by copolymerization with other materials.[32–39] The block copolymerization method, in particular, results in new polymers, keeping the original properties of the starting materials. Recently, Kawai et al. reported that high molecular weight polyethers are degradable by microorganisms.[40] Therefore, the block copolymerization of the copoly(SA/EO)s with a polyether is interesting in terms of producing a novel biodegradable polymer. In this work, we aimed to synthesize a biodegradable block copolymer of copoly(SA/EO) with polyether and to clarify the relationship between biodegradability or thermal properties and the molecular weight or the composition of the copoly(SA/EO)s.

EXPERIMENTAL

Materials

SA (from Wako Pure Chemical Co., Osaka, Japan) was recrystallized from chloroform. EO (from Sumitomo Seika Co., Osaka, Japan) was distilled over CaH_2 under reduced pressure. Polyethers [poly(ethylene glycol) (PEG)] and [poly(propylene glycol)(PPG)] and titanium triisopropoxide (TIP) were used as purchased from Wako Pure Chemical Co. The enzymes for the biodegradation tests were lipases from *Rhizopus arrhizus* (Boehringer Mannheim, Mannheim, Germany) and from *Rhizopus delemar* and *Candida cylindracea* (Seikagaku Kogyo, Tokyo, Japan). Standard activated sludge was from the Chemical Inspection & Testing Institute, Japan.

Synthesis of Copoly(SA/EO) (Scheme 1)

A series of copoly(SA/EO)s were prepared by a ring-opening copolymerization technique described in detail elsewhere.[30] A representative example of a chain-extension reaction of copoly(SA/EO)s is the following one: The copolymer (3 g) and PEG (3 g) were placed in a 100-mL flask equipped with a stirrer. After the copolymer was melted by heating and dried for 30 min at 150°C *in vacuo* in order to remove the water, TIP (0.025 g) was added and stirred under a vacuum at 170°C for 3–12 h. The products were dissolved in chloroform. Insoluble materials were removed by filtration. The chloroform solution was concentrated *in vacuo.* The polymers were precipitated from the chloroform solution with petroleum ether and dried under a vacuum at 80°C for 24 h.

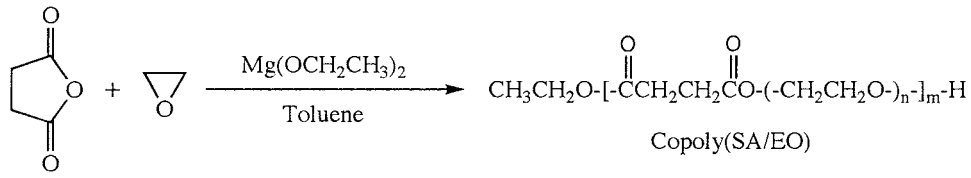
Preparation of Films

Film specimens of thickness 50–100 μm were formed by compression molding of polymer powder or flake using a laboratory press (G-12, Techno Supply Co., Ltd., Japan) at the melting temperature of the copolymers for 30 s at 50 kg/cm^2. The prepared films were aged for at least 7 days at room temperature to reach equilibrium crystallinity.

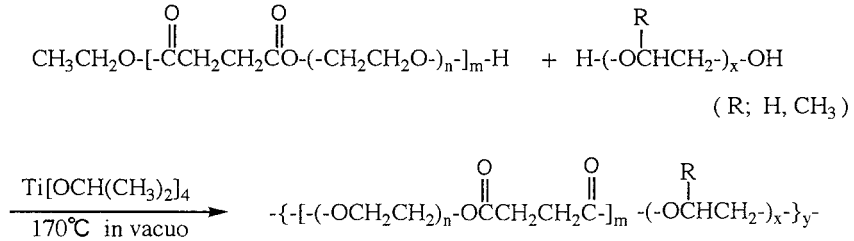
Enzymatic Degradation

Enzymatic hydrolysis tests were carried out as follows: Twenty-five milligrams of the polymer samples and 2 mL of phosphate buffer (KH_2PO_4/Na_2HPO_4, pH 7.0) were placed in a test tube, and the prescribed units of the enzyme were added. Blank tests were conducted for the polymers suspended without the enzyme and for the enzyme itself. The enzymes used were lipase from *R. arrhizus, R. delemar,* and *C. cylindracea.* The enzymatic hydrolysis tests were carried out at 37°C for a fixed time. After filtration (0.2-μm membrane filter), the total organic carbon (TOC) of the filtrate was measured with a TOC analyzer (Shimadzu TOC500). The net TOC values were calculated by subtracting the average values at the two control tests from the average of two measurements.

Ring-opening copolymerization of succinic anhydride with ethylene oxide



Polycondensation of copoly(SA/EO) and polyethylene glycol or polypropylene glycol



Scheme 1

Degradation by Activated Sludge

A schematic diagram of the apparatus for an aerobic degradation test was described in detail elsewhere.[30] The supernatant (30 mL, MLSS, 30 mg) of standard activated sludge and a polymer sample (0.2 g) were placed in a fermenter containing a carbon-free culture medium (500 mL, pH 7) according to ASTM D5209-92. The fermenter was incubated at 30°C and aerated with CO_2-free air under magnetic stirring. The evolved CO_2 was absorbed into a 0.5% sodium hydroxide solution and determined by an inorganic carbon concentration (IC) measurement for the alkaline solution with a TOC analyzer at specific times until the evolution rate reached a plateau. Biodegradation (%) of the polymers was calculated from the following equation:

$$\text{Biodegradation (\%)} = [(\text{experimentally measured } CO_2)/(\text{theoretical } CO_2)] \times 100$$

Theoretically released CO_2 was calculated from the chemical structural formula of these copolymers by assuming that oligomers or monomers, first formed by enzymatic hydrolysis, completely mineralized to CO_2.

Analytical Procedures: Characterization of Copolymers

^{1}H-NMR spectra were recorded on a JEOL JNM A-500 spectrometer (500 MHz). All spectra were obtained from chloroform-*d* solutions at room temperature with TMS as the internal standard. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer using film samples cast on a potassium bromide plate from chloroform solutions. Differential scanning calorimetry (DSC) measurements were conducted with a Seiko Denshi DSC120 for the sample from 4 to 8 mg at a heating rate of 10°C/min in the range of temperature from −60 to 120°C (first scan). After the first run, the sample was cooled to −60°C at a rate of ca. 10°C/min, followed by second run under the same conditions. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were determined with a GPC (TOSOH, HCL-8020). The columns were a TSKgel G4000HXL and a TSKgel G3000HXL with a limited exclusion molecular weight of 4×10^5. Chloroform was used as an eluent at a flow rate of 0.6 mL/min. Polystyrene standards with low polydispersities were used to generate a calibration curve.

RESULTS AND DISCUSSION

Block Copolymerization

Two kinds of copoly(SA/EO)s, SA content 42–43 or 48–49 mol %, as a prepolymer for polycondensation

were synthesized by the ring-opening copolymerization of SA with EO by varying the feed comonomer ratio. Commercial polyether, PEG2000, PEG6000, PPG1000, and PPG3000, were used as materials. Figure 1 shows ^{1}H-NMR spectra of the copolymers of copoly(SA/EO) with (b) PEG6000 or with (c) PPG3000 together with (a) one of copoly(SA/EO)s, SA/EO = 48/52 mol %, M_n = 11700, used as a prepolymer.

^{1}H-NMR spectra of the copolymer synthesized from copoly(SA/EO) and PEG6000 showed that the signal of methylene protons of PEG was added to the spectrum of the original copoly(SA/EO). The signals of methylene proton [—OCH($C\underline{H}_3$)-CH_2O—, δ = 1.15 ppm, —OCOCH($C\underline{H}_3$)$C\underline{H}_2$—, δ = 1.25 ppm] and methyne proton [—OCOC$\underline{H}$-(CH_3)CH_2—, δ = 5.15 ppm] were further found in the ^{1}H-NMR spectrum of the copolymers of copoly(SA/EO) with PPG3000 [Fig. 1(c)]. Figure 2 shows the DSC curves of typical copolymers. The DSC curves (a) of the copolymers, SA/EO = 28/72, M_n = 58000, synthesized by the polycondensation of copoly(SA/EO), SA/EO = 42/58, M_n = 4300, with PEG6000 showed two endotherm peaks at the first run. The lower-temperature endotherm peak was attributed to the crystalline fusion of the PEG6000 and the higher-temperature endotherm peak was due to the that of copoly(SA/EO). On the other hand, one endotherm peak due to the crystal fusion of copoly(SA/EO) was shown in the DSC curve of the copolymer synthesized by the polycondensation of copoly(SA/EO), SA/EO = 49/51, M_n = 11700, with PPG1000 [Fig. 2(b, c)]. The T_m of the copolymer including 7 mol % of the propylene glycol (PG) component was similar to that of the copoly(SA/EO) used as a prepolymer and the endotherm peak shifted to lower temperatures and broadened only with an increase in PG content. Furthermore, the result of the GPC measurement of these polymers showed a single-modal curve. These results indicate that the obtained copolymers are block copolyesterethers.

The results of the block copolymerization of copoly(SA/EO) with PEG are summarized in Table I. When a low SA content of copoly(SA/EO), SA/EO = 42/58 or 43/57 mol %, was used as a prepolymer, the yields of the polycondensates were a range of 70–90%. The polymer composition, SA/[EO + ethylene glycol (EG)], of these block copolymers were similar to the ones calculated from the amount of the feed prepolymers. The M_ns of the block copolymers increased with increase in the feed ratio of PEG to the copoly(SA/EO). The molecular weight distribution (M_w/M_n) increased slightly, at high (EO + EG) contents, compared to that of the copoly(SA/EO) used as a prepolymer. When the feed ratio of copoly(SA/EO) to PEG was rich (run 2), the yield of the produced copolymer reached 91 wt % and the polymer composition of the obtained block copolymer was the same as that of the feed prepolymers. Furthermore, in the case of the low feed ratio of copoly(SA/EO) to PEG (run 3), the results were similar to that described above (run 2). The M_ns of the both block copolymers (runs 2 and 3) were more than those of the ABA-type block copolymers between copoly(SA/EO) and PEG. These results suggest that the chain-extension reaction of copoly(SA/EO) or PEG itself takes place in addition to the polycondensation between copoly(SA/EO) and PEG and the obtained copolymers were multiblock copolymers.

There was no endotherm peak in the DSC curve of the block copolymer produced at a low feed molar ratio of PEG2000 to the copoly(SA/EO), SA/EO = 42/58, M_n = 4300 (run 1 in Table I). When the feed ratio of PEG2000 was higher than 72 mol %, the endotherm peak calculated from the crystal fusion of PEG2000 was observed (run 3). By using PEG6000, two endotherm peaks based on the crystalline fusion of the both prepolymers appeared (run 2). With an increase in the molar ratio of PEG6000, one endotherm peak was observed and the fusion heat (ΔH) was larger than that recorded for other three copolymers (run 4). It is thought that this endotherm peak is overlapped by two different peaks based on the crystalline fusion of copoly(SA/EO) and PEG6000. The glass transition (T_g) of the block copolymer shifted to lower temperatures compared to that of copoly(SA/EO) as a prepolymer and one of the chain-extended copoly(SA/EO), T_g = −16°C. The T_g of the block copolymers showed a similar trend by being shifted to lower temperatures with increase in the feed molar ratio of PEG to copoly(SA/EO) (runs 2 and 4).

In general, a block copolymer synthesized from incompatible materials is known to exhibit a microphase-separation structure. A block copolymer synthesized from two different amorphous polymers has two different T_gs in the neighborhood of the T_gs of both prepolymers. The block copolymers from two crystalline prepolymers, copoly(SA/EO) and PEG, had a small T_g width based on copoly(SA/EO) in the DSC second run. The above-mentioned T_g of the block copolymers showed a significant drop compared to that of co-

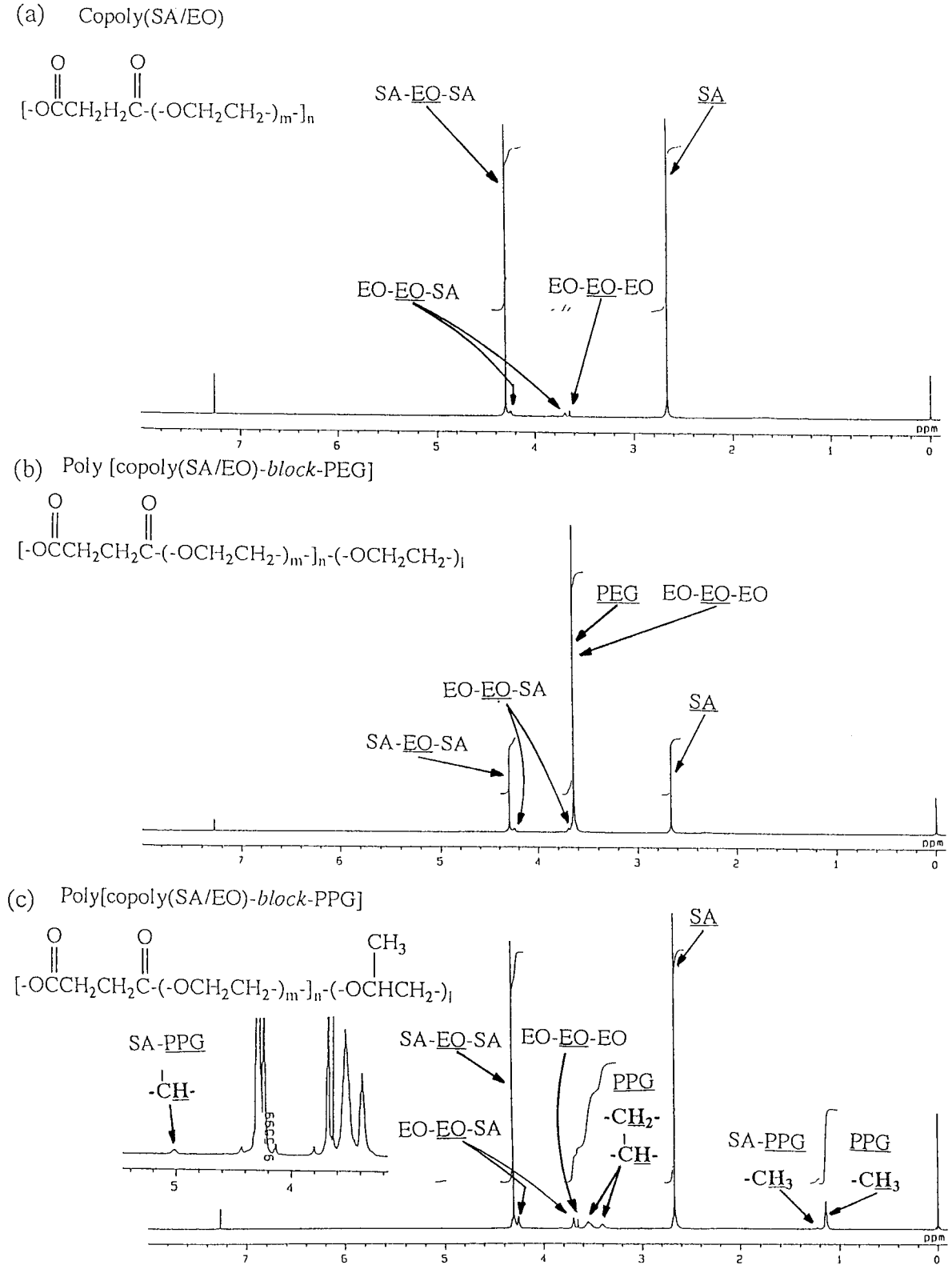


Figure 1 ^{1}H-NMR spectra of the copolymers: (a) prepolymer, copoly(SA/EO), M_n = 11700, SA/EO = 48/52 mol %; (b) block copolymer of copoly(SA/EO) with PEG6000, M_n = 125,000, SA/[EO + EG] = 17/83 mol %; (c) block copolymer of copoly(SA/EO) with PPG3000, M_n = 39,000, SA/EO/PG = 37/47/16.

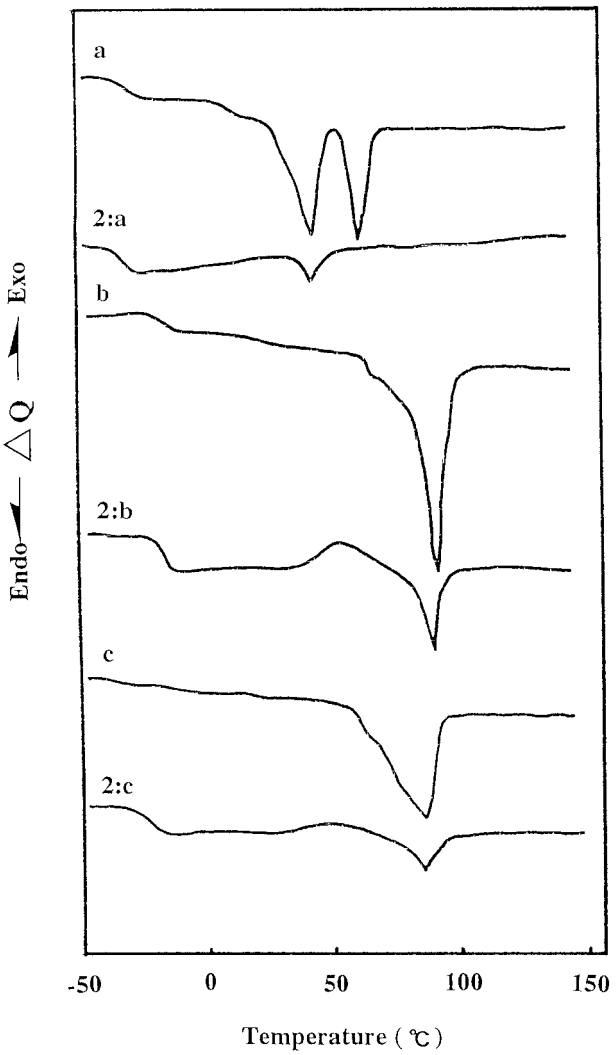


Figure 2 DSC curves of typical copolymers: (a) block copolymer, M_n = 58,000, SA/(EO + EG) = 28/72 mol %; (b) block copolymer, M_n = 62,000, SA/EO/PG = 43/50/7; (c) block copolymer, M_n = 74,000, SA/EO/PG = 33/46/21. (2) Second run, 10°C/min cooling from the melt.

poly(SA/EO) itself. The shift width of the T_g to lower temperature was approximately 20°C. This result is in favor of our assumption that the PEG segments and copoly(SA/EO) were well compatible and can be mixed in the amorphous phase of copoly(SA/EO) without any microphase separation in the solid state. The compatibility of both polymers, however, would not be so high as to prevent crystallization of both polymers. In addition, the ΔH of the block copolymers was found to increase with increase in the M_n of PEG. An increase in the M_n of PEG induced further crystallization in the block copolymers.

In the case of the polycondensation of copoly(SA/EO), SA/EO = 48/52 or 49/51 mol %, with PEG, the polymer yields were around 80 wt % and the compositions of the obtained copolymers were of compositions similar to those of the feed prepolymers. These results were consistent with those obtained by using a low SA content of copoly(SA/EO). The M_ns of these copolymers increased with increase in the copoly(SA/EO) content. The two endotherm peaks were observed in DSC curves for these copolymers except for the copolymer where a large excess of PEG2000 was used (run 8). These results indicate that increase in the SA content in copoly(SA/EO) or in the M_n of PEG tends to enhance the crystallinity in the obtained block copolymers. The T_g of the block copolymer varied from −35 to 37°C and the changes in the T_g versus the M_n of the prepolymer were small compared to the one using an SA content 42–43 mol % of copoly(SA/EO).

Table II shows the yields of the polycondensation of copoly(SA/EO) with PPG. The yields of the produced polymer were within a range of 70 wt % except for the case of higher feed molar ratio of PPG3000 to copoly(SA/EO) (run 4 or 8). The composition of these block copolymers varied substantially compared to those of feed prepolymers. When PPG3000 was used as a prepolymer, the yield of the copolymers was lower compared to that of polymerized PPG1000. A possible explanation regarding the different behavior of PPG1000 and PPG3000 is that the low molecular weight copolymers including the long-chain length of PPG are likely to be removed by precipitation using petroleum ether. The M_ns of these copolymers increased with increase in the M_ns of the copoly(SA/EO)s. The M_w/M_ns of these copolymers were within the same range as those of prepolymers. The T_m of these copolymers was low compared to that of the prepolymers. The lowering of the T_m became more pronounced as the PG content in the block copolymer increased and the SA content in copoly(SA/EO) decreased. The ΔH of these copolymers decreased with increase of the PG content. The T_g of these copolymers remained almost unchanged compared to that of the chain-extended copoly(SA/EO) (run 5 or 11 in Table I). The latter observation strongly suggests that the block copolymers from copoly(SA/EO) and PPG have a microphase-separation structure. However, since the shift width of the T_g of the block copolymer having SA/EO/PG = 33/46/21 was about 4°C (run 7 in Table II) compared to that of the copoly(SA/EO) and the DSC curve of the

Table I Results of Block Polymerization of Copoly(SA/EO) and PEG

	Copoly(SA/EO)			Feed Ratio		Block Polymer							
Run	Composition[a] SA/EO (mol %)	M_n[b]/10^4	PEG M_n/10^4	Copoly(SA/EO)/PEG (mol %)	Unit Ratio SA/(EO + EG) (mol %)	Yield (%)	Unit Ratio[a] SA/(EO + EG) (mol %)	M_n[b]/10^4	M_w/M_n	T_m[c] (°C)	ΔH[d] (J/g)	T_g[e] (°C)	Biodegradation TOC[f] (ppm)
1	42/58[g]	0.43	0.20	58/42	28/72	79	27/73	3.4	2.6	ND	—	−30	30
2	42/58[g]	0.43	0.60	81/19	28/72	90	28/72	5.8	2.4	46, 66	31, 16	−27	20
3	43/57[h]	0.51	0.20	28/72	17/83	71	19/81	5.8	2.0	38	30	−37	430
4	43/57[h]	0.51	0.60	54/46	17/83	81	16/84	8.2	1.7	61	75	−36	0
5	42/58	0.45	—	100/0	42/58	85	42/58	3.3	1.9	75	43	−16	2000
6	48/52[h]	0.33	0.20	38/62	19/81	79	18/82	5.4	2.0	38, 72	27, 17	−35	50
7	48/52[h]	0.33	0.60	65/35	19/81	82	17/83	5.7	2.1	53, 80	82, 25	−37	10
8	49/51[j]	1.17	0.20	15/85	19/81	85	18/82	6.7	2.1	68	190	−36	100
9	49/51[j]	1.17	0.60	34/66	19/81	63	17/83	6.0	2.1	50, 83	45, 21	−36	60
10	48/52[k]	2.50	0.60	19/81	18/82	83	18/82	7.3	1.6	51, 93	47, 14	−35	30
11	48/52[j]	1.17	—	100/0	48/52	60	48/52	8.7	1.8	94	47	−16	20

$Ti[OCH(CH_3)_2]_4$ was used as a catalyst under a vacuum at 170°C for 7 h.

[a] Determined by ^{1}H-NMR.

[b] Determined by GPC.

[c] Determined by DSC. The peaks underscored had disappeared at the second scan.

[d] Determined by DSC first scan.

[e] Determined by DSC second scan.

[f] Total organic carbon of the water-soluble compounds produced by enzymatic degradation using the lipase from *R. arrhizus*. TOC value after subtraction of their blank levels were tabulated.

[g] T_g = −28°C.

[h] T_g = −25°C.

[i] T_g = −20°C.

[j] T_g = −15°C.

[k] T_g = −16°C.

Table II Results of Block Polymerization of Copoly(SA/EO) and PPG

	Copoly(SA/EO)			Feed Ratio		Block Polymer							
Run	Composition[a] SA/EO (mol %)	M_n[b]/10^4	PPG M_n/10^4	Copoly(SA/EO)/PPG (mol %)	Unit Ratio SA/EO/PG (mol %)	Yield (%)	Unit Ratio[a] SA/EO/PG (mol %)	M_n[b]/10^4	M_w/M_n	T_m[c] (°C)	ΔH[d] (J/g)	T_e[e] (°C)	Biodegradation (TOC[f]) (ppm)
1	42/58[g]	0.43	0.10	41/59	30/42/28	75	48/27/25	2.5	2.1	51	30	−25	1350
2	42/58[g]	0.43	0.30	68/32	30/42/28	56	54/34/12	2.2	1.7	59	28	−16	250
3	43/57[h]	0.51	0.10	16/84	20/26/54	67	16/40/44	4.5	2.4	56	3	−45	310
4	43/57[h]	0.51	0.30	37/63	20/26/54	28	29/44/27	6.2	2.0	83	38	−16	300
5	49/51[i]	1.17	0.10	50/50	22/23/55	78	43/50/7	6.2	2.1	93	49	−14	90
6	49/51[i]	1.17	0.30	50/50	22/23/55	73	37/47/16	3.9	2.5	93	49	−13	10
7	49/51[i]	1.17	0.10	25/75	10/11/79	71	33/46/21	7.4	2.4	87	42	−19	420
8	49/51[i]	1.17	0.30	25/75	10/11/79	33	35/57/8	8.3	1.8	98	56	−14	60
9[j]	—	0.80	—	100/0	45/45/10[k]	84	45/45/10[k]	3.9	1.9	64	29	−14	660

$Ti[OCH(CH_3)_2]_4$ was used as a catalyst under a vacuum at 170°C for 7 h.
[a] Determined by ^{1}H-NMR.
[b] Determined by GPC.
[c] Determined by DSC. The peaks underscored had disappeared at the second scan.
[d] Determined by DSC first scan.
[e] Determined by DSC second scan.
[f] Total organic carbon of the water-soluble compounds produced by enzymatic degradation using the lipase from *R. arrhizus*. TOC values after subtraction the blank levels.
[g] $T_g = -28$°C.
[h] $T_g = -25$°C.
[i] $T_g = -15$°C.
[j] Copoly(SA/EO/PO) synthesized by ring-opening copolymerization was used.
[k] Molar ratio SA/EO/PO.

block copolymer showed the broad endotherm peak [Fig. 2(c)], it is deduced that an increase in the PG content prevents the formation of a microphase-separation structure. The thermal properties of the block copolymers synthesized from the copoly(SA/EO) and PPG were remarkably different from those of the terpoly[SA/EO/propylene oxide (PO)] prepared by the ring-opening terpolymerization of SA, EO, and PO.[29] It is presumed that these phenomena were caused by inherent differences both in the crystal structures and in the crystal sizes of the copolymers which are either random copolymers or block copolymers, containing PO as third component except for SA and EO.

Enzymatic Degradation

The results of the enzymatic degradation testing (TOC values) of the block copolymers of copoly(SA/EO) with PEG or PPG by the lipase from *R. arrhizus* are shown in Tables I and II, respectively. We have previously reported that the enzymatic degradability of the copoly(SA/EO)s, used as a prepolymer, decreased drastically with increase in the SA content.[29,30] As a prepolymer, copoly(SA/EO)s both of high and low degradability (runs 1–5 and runs 6–11, from Table I, respectively) were used. The data on the copolymers after the chain-extension reaction of copoly(SA/EO) itself are shown at runs 5 and 11 in Table I.

If one compares runs 1–4 to run 5 in Table I, the biodegradability of the block copolymer of high biodegradable copoly(SA/EO)s with PEGs is found to decrease significantly irrespective of the M_n of PEG compared to that of the extended copoly(SA/EO) itself.

The enzymatic degradation of the copolyesterethers gave a higher value with increase in the feed ratio of PEG2000 to the copoly(SA/EO) (run 3). No endotherm peak was recorded in the DSC curve for the run 1 copolymer. On the other hand, only one endotherm peak based on a PEG segment was observed in the DSC curve for the run 3 copolymer. However, an increase in the M_n of PEG drastically decreased the enzymatic degradability of the block copolymer (run 4).

Table II shows the results of the enzymatic degradation testing of block copolymers of copoly(SA/EO) with PPG. Highly biodegradable copoly(SA/EO)s, as a prepolymer, was used for runs 1–4, whereas for runs 5–8, nonbiodegradable copoly(SA/EO) were. The decrease in enzymatic degradability of the block copolymer of the highly biodegradable copoly(SA/EO) with PPG was smaller than that of the block copolymer including PEG, although the enzymatic degradability decreased with increase of the PG content in the block copolymers. This reverse tendency was observed in the case of the block copolymer of copoly(SA/EO) with PEG. Moreover, the fusion heat (ΔH) of the run 3 copolymers was lower than the one of the run 1 copolymer. This result indicates that the enzymatic biodegradability of the block copolymer was not influenced by the crystalline area.

The results of the enzymatic degradation of the block copolymer of the nondegradable copoly(SA/EO) with PPG (from runs to 8 in Table II) showed that the degradability of the block copolymers was higher than that of the chain-extended copoly(SA/EO) itself and also higher than that of the block copolymer of copoly(SA/EO) with PEG (from run 5 to 10 in Table I).

The enzymatic degradability of the block copolymers containing PPG1000 was larger than that of the block copolymers including PPG3000 and increased with increase in the feed ratio of PPG. The results of introducing a methyl group as a side-group chain in the main polymer chain on the biodegradation have been reported.[41] We have also studied the degradation of the terpoly(SA/EO/PO), synthesized by the ring-opening terpolymerization of SA, EO, and PO, and reported that the enzymatic degradability of the terpoly(SA/EO/PO), with PO content higher than 10 mol %, decreased with increase in the PO content.[42] The TOC value, due to formation of water-soluble compounds after enzymatic hydrolysis, of the block copolymer with 21 mol % content of PG was equal to 420 ppm. The introduction of more than 21 mol % of PG resulted in a significant decrease of the degradability (run 3 in Table II) because of the methyl group. The chemical structures of the block copolymers synthesized by the polycondensation of copoly(SA/EO) with PPG were of almost identical composition as that of the terpoly(SA/EO/PO). However, the block copolymers including 20 mol % PG maintained the T_m of the copoly(SA/EO), used as a prepolymer, and exhibited high biodegradability, in contrast to less than 10 mol % PG for the terpoly(SA/EO/PO). Therefore, it can be concluded that the block copolymerization is superior to the terpolymerization regarding the optimum combination of prepolymer properties in the resulting polymer such as the biodegradability and the thermal and mechanical properties. This result may be interpreted as follows: The block copolymers synthesized

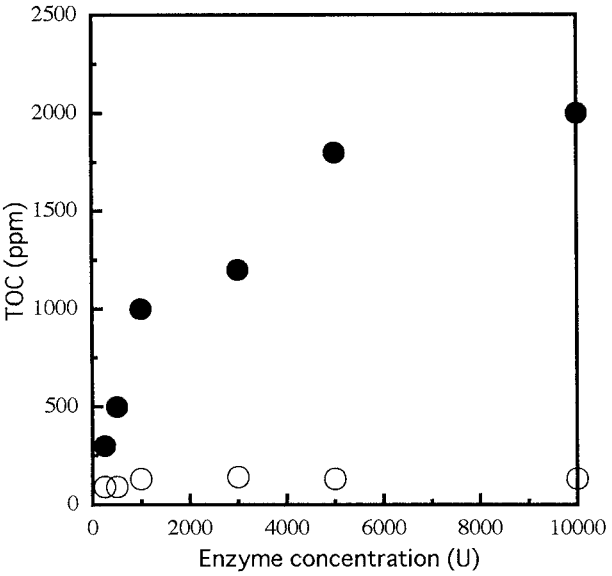


Figure 3 Relationship between TOC of water-soluble compounds produced by enzymatic degradation and enzyme activity: (○) block copolymer of copoly(SA/EO) with PEG (M_n = 2000), M_n = 30,000, SA/(EO + EG) = 42/58 mol %; (●) block copolymer of copoly(SA/EO) with PPG (M_n = 1000), M_n = 74,000, SA/EO/EG = 33/46/21 mol %.

by the polycondensation of copoly(SA/EO) with polyether have a near microphase-separation structure with an overlapping of both segments in the amorphous region. As a result, the compatibility of both segments in the amorphous region will bring a change of the crystalline structure and results in increasing the enzymatic biodegradability. This finding was also confirmed by the DSC curves where the endotherm peaks became broader and a shoulder occurred after the block copolymerization.

Figure 3 shows the relationship between the enzymatic degradability of the two block copolymers of run 2 (Table I) and run 7 (Table II) versus the enzyme concentration with variation from 250 to 10,000 U. The enzymatic degradability of the block copolymer, synthesized using copoly(SA/EO) and PEG, was small, independent of the enzyme concentration. On the other hand, the degradability of the block copolymer including copoly(SA/EO) and PPG increased remarkably with increase in the enzyme concentration.

Table III shows the enzymatic degradability of three block copolymers of varying polymer composition by three kinds of the lipases from *R. arrhizus, R. delemar,* and *C. cylindracea.* The enzymatic degradability decreased in the above-mentioned order always irrespective of their polymer composition. In particular, the degradability of the block copolymer including PPG by the lipase from *R. arrhizus* proved to be the highest in all runs in Table III. This result is in agreement with the tendency already reported in the case of the chain-extended copoly(SA/EO) having 42 mol % SA content.[30]

Degradation by Activated Sludge

Studies on the biodegradation of the block copolyesterethers, synthesized by polycondensation of copoly(SA/EO) with PEG or PPG, were carried out using a standard activated sludge. Figure 4 shows the results of the biodegradation estimated from the amount of the evolved CO_2 (IC measurements, experimental values after subtraction of the control test values). Seventy weight percent of the chain-extended copoly(SA/EO) (polymer composition SA/EO = 42/58, M_n = 45,000) was converted into CO_2 for 28 days. In the case of the block copolyesterether [polymer composition SA/(EO + EG) = 35/65, M_n = 75,000] of copoly(SA/EO) with PEG6000, 17 wt % of the copolymer was converted into CO_2 under the same conditions. The biodegradation rates of the block copolyesterethers of copoly(SA/EO)s with PPGs were intermediate between that of the highly degradable extended copoly(SA/EO) and that of the block copolyesterethers of copoly(SA/EO) with PEG6000. This tendency of biodegradability of the copolymers evaluated by the activated sludge method was similar to that of enzymatic hydrolysis by a lipase. The biodegradability of the block copolyesterether of copoly(SA/EO) with PPG gave higher values with increase in the PG content of the copolymers. The part (10 mL) of the medium including the polymer sample and the standard activated sludge was taken up every week and filtered though 5A filter paper and the TOC based on the water-soluble products in the filtrate was measured. The results are shown in Figure 5. In the case of the biodegradable chain-extended copoly(SA/EO), the TOC values, which were 10 ppm after 6 days, decreased with time and nearly reached a zero value. Thus, it is fair to suggest that the copoly(SA/EO) is first enzymatically hydrolyzed by activated sludge microbes, followed, at a later stage, by the conversion of the released water-soluble compounds, monomers or oligomers, to CO_2. In contrast, the compounds from the hydrolysis of the block copolyesterethers of copoly(SA/EO) with polyether were not completely converted to CO_2. These results were fur-

Table III Enzymatic Degradation of Block Copolymer by Three Kinds of Lipase

Run	Block Copolymer: SA/(EO + EG) or SA/EO/PG (mol %)	Block Copolymer: $M_n/10^4$	Enzymatic Degradation, TOC (ppm): *R. arrhizus*	*R. delemar*	*C. cylindracea*
1	28/72	3.6	60	40	30
2	48/27/25	2.5	1300	430	170
3	43/50/7	6.2	300	70	10

Enzyme activity, 250 U for 24 h at 37°C.

ther confirmed by the fact that the TOC values were constantly independent of the elapsed time. The TOC values for the block copolyesterether including PPG3000 were unexpectedly low because of the limited solubility of the hydrolyzed compound in the phosphate buffer solution.

CONCLUSIONS

The thermal properties and the biodegradation of the block copolyesterethers, synthesized by the polycondensation of the copoly(SA/EO) prepared by the ring-opening copolymerization of SA with EO and commercially available polyether, were investigated and characterized as follows:

1. The block copolyesterethers including nonbiodegradable copoly(SA/EO), high SA content, and polyether were found to become biodegradable without undergoing any change in the T_m and ΔH of the original prepolymers.
2. Although, the block copolyesterethers includ-

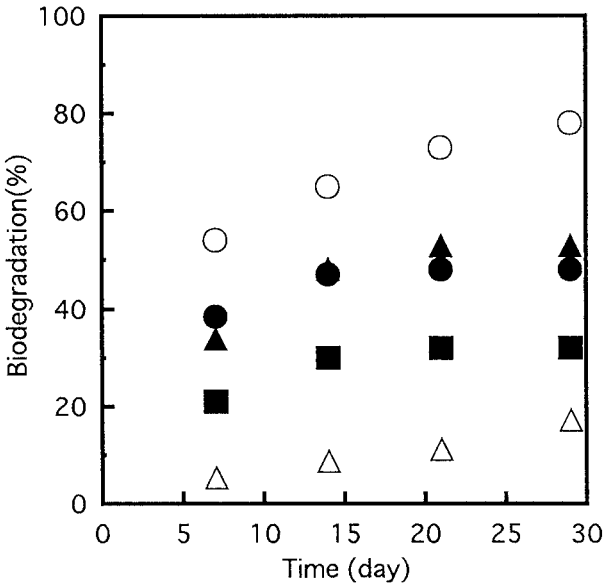


Figure 4 Biodegradation of copolymers by activated sludge at 30°C: (○) chain-extended copoly(SA/EO), M_n = 33,000, SA/EO = 42/58 mol %; (△) block copolymer of copoly(SA/EO) with PEG6000, M_n = 82,000, SA/(EO + EG) = 43/57 mol %; (■) block copolymer of copoly(SA/EO) with PPG1000, M_n = 62,000, SA/EO/PG = 43/50/7 mol %; (●) block copolymer of copoly(SA/EO) with PPG3000, M_n = 39,000, SA/EO/PG = 37/47/16 mol %; (▲) block copolymer of copoly(SA/EO) with PPG1000, M_n = 74,000, SA/EO/PG = 33/46/21 mol %.

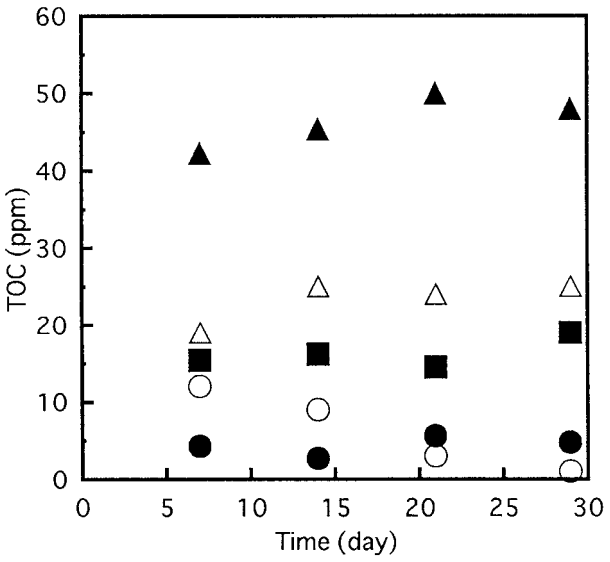


Figure 5 TOC based on water-soluble compounds produced by activated sludge (in incubator): (○) chain-extended copoly(SA/EO), M_n = 33,000, SA/EO = 42/58 mol %; (△) block copolymer of copoly(SA/EO) with PEG6000, M_n = 82,000, SA/(EO + EG) = 43/57 mol %; (■) block copolymer of copoly(SA/EO) with PPG1000, M_n = 62,000, SA/EO/PG = 43/50/7 mol %; (●) block copolymer of copoly(SA/EO) with PPG3000, M_n = 39,000, SA/EO/PG = 37/47/16 mol %; (▲) block copolymer of copoly(SA/EO) with PPG1000, M_n = 74,000, SA/EO/PG = 33/46/21 mol %.

ing PPG had a microphase-separation structure, the biodegradability increased with increase in the PG content less than 20 mol %.
3. The biodegradability of the block copolyesterethers was independent of the composition of the copolymers under both evaluations by lipase and by activated sludge.
4. The oligomers, mainly including polyether used as a prepolymer, reproduced by degradation using activated sludge, remained in the system without further degradation.

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