

Synthesis and Biodegradation of Copolyesterether of Copoly(Succinic Anhydride/Ethylene Oxide) with Triblock Copolymer of Poly(oxyethylene)-Poly(oxypropylene)-Poly(oxyethylene)

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ABSTRACT: The thermal properties and biodegradability of the block copolyesterethers with copoly[succinic anhydride (SA)/ethylene oxide (EO)], synthesized by ring-opening copolymerization as a hard segment and the triblock copolyethers of poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) (PN) as a soft segment, were studied. The block copolyesterethers synthesized from higher than 8000 number-average molecular weight (M_n) of copoly(SA/EO)s showed a microphase separation structure as determined by the thermal properties [melting point (T_m) and glass transition (T_g)], at any polymer composition [EO/propylene oxide (PO)] or the determination of M_n of PN. A decrease in the M_n of copoly(SA/EO) or an increase in PO content in PN resulted in depression of heats of fusion (ΔH) of these block copolyesterethers. The enzymatic degradation of the block copolyesterethers by the lipase from *Rhizopus arrhizus* showed a substantial increase with a decrease in their ΔH , whereas it was depressed with an increase in the M_n of polyoxyethylene or polyoxypropylene segment in the block copolyesterethers. The block copolyesterethers were degraded by microorganisms in activated sludge. The biodegradability of the block copolyesterethers showed a pronounced drop, with an increase in the polyoxyethylene chain length or polyoxypropylene content in PN. The polycondensation was also conducted without a catalyst at 190°C, similarly, to the reaction catalyzed with $Ti[OCH(CH_3)_2]_4$ at 170°C. The effect of the residual titanium on the biodegradability of the block copolyesterethers was negligible.
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Key words: biodegradation; block copolyesterether; enzyme; activated sludge; differential scanning calorimetry; microphase separation structure

INTRODUCTION

Although polymer industries have long been oriented toward the production of “recalcitrant,” not

easily decomposed or degraded polymers, the current demand for easy disposal of synthetic polymers has instigated many investigations on recycling, composting, and synthesis of biodegradable polymer or blends.^{1,2} Three different ways have been put forward for addressing the issue of biodegradability³: synthetic polymer/biopolymer mixtures, microbial polymers produced by fermenta-

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tion, and agricultural polymer used directly as a basic packaging material.^{4,5} There have been many problems related to the large-scale use on synthetic polymers and plastic products. Because almost the majority of conventional polymers are not biodegradable, parts of them have been accumulated as a litter in the environment during their waste treatments. Furthermore, recycling and reuse of these polymers inevitably result in a lowering of the quality of utility goods. Biodegradable synthetic polymers are considered to be a promising approach toward solving environmental problems and, as such, they have been extensively studied by many researchers.^{6–39} Biodegradable polymers, such as poly(ϵ -caprolactone),^{6,7} poly(butylene succinate),⁸ and polylactides,^{9–21} either have already been on the market or are on the point of being commercialized. There have been many attempts to put these polymers into practical use in various fields and to make the best possible use of their thermal properties. The block copolymerization^{15–21} of several biodegradable polymers with other materials, polymers, or monomers, is considered as one of the standard methods for preparing “tailor-made” polymers.

The block copolymerization of copoly[succinic anhydride (SA)/ethylene oxide (EO)], synthesized by the ring-opening copolymerization of SA and EO—with polyethers such as polyethylene glycol or polypropylene glycol (PPG)—has already started and is an ongoing research project. Furthermore, the relationships between the biodegradability, the thermal properties of their block copolyesterethers, and the composition of the copoly(SA/EO) and/or the M_n of two prepolymers and the feed molar ratio of the two prepolymers were investigated and reported.⁴⁰ The synthesized block copolyesterethers showed a microphase separation structure on the basis of their thermal properties [i.e., melting point (T_m) and glass transition (T_g)] by differential scanning calorimetry (DSC). The lower M_n of PPG is compatible with copoly(SA/EO), and the biodegradability of the obtained block copolyesterethers was greatly enhanced with high PPG content.

Recently, Kimura and colleagues^{16–18} have reported the polycondensation of poly(L-lactide) with triblock[poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene)] (PN) (PluronicTM; PN from Asahi Denka Co., Ltd., Japan), thus managing to improve the mechanical properties of poly(L-lactide).

In this article, the aim was to synthesize a bio-

degradable block copolymer of copoly(SA/EO)s with PN to improve the mechanical properties of copoly(SA/EO)s and to clarify the relationships between their biodegradability, their thermal properties, and the M_n and/or the composition of the two prepolymers.

EXPERIMENTAL

Materials

SA (from Wako Pure Chemical Co. Ltd., Japan) was recrystallized from chloroform. EO (from Sumitomo Seika Co. Ltd., Japan) was distilled over CaH₂ under reduced pressure. The trade names, the general formulas, and the M_n 's of the studied PN are given in Table I. They were kindly supplied by Asahi Denka Co. Ltd., Japan. Titanium tri-*iso*-propoxide (TIP) and other chemicals were used as purchased from Wako Pure Chemical Co. The enzyme for the biodegradation testings was the lipase from *Rhizopus arrhizus* (Boehringer Mannheim, Mannheim, Germany). Standard activated sludge was offered from 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.³⁸ A representative example of a chain-extension reaction of copoly(SA/EO)s is as follows: the equimolar amounts of copoly(SA/EO) and PN were placed in a 100-ml flask equipped with a stirrer. After the copolymer was molten by heating and dried for 30 min at 150°C *in vacuo* to remove water, TIP (0.025 g) was added and the mixture was kept stirring under vacuum at 170°C for 3–12 h. Products were dissolved in chloroform and insoluble materials were removed by filtration. The chloroform solution was concentrated *in vacuo*. Polymers were precipitated from the chloroform solution with petroleum ether and dried under vacuum at 80°C for 24 h.

Preparation of Films

The film specimens, of the copolymer powder or flake (thickness: 50–100 μm) were formed by compression molding using a laboratory press (G-12, Techno-Supply Co. Ltd., Japan) at the melting temperature of the copolymers for 30 s at 50 kg/

Table I Trade Names, General Formulas, Polymer Composition and Number-Average Molecular Weights of the Studied (EO)_x(PO)_y(EO)_x Block Copolymers (Pluronic)

Pluronic	General Formula	Polymer Comp. EO/PO (mol %)	Number-Average Molecular Weight
L31	(EO) ₂ (PO) ₁₆ (EO) ₂	20/80	1100
L61	(EO) ₃ (PO) ₃₀ (EO) ₃	17/83	2000
L44	(EO) ₁₁ (PO) ₂₁ (EO) ₁₁	51/49	2200
L121	(EO) ₇ (PO) ₆₆ (EO) ₇	17/83	4500
F68	(EO) ₇₅ (PO) ₃₀ (EO) ₇₅	83/17	8350
P85	(EO) ₂₇ (PO) ₃₉ (EO) ₂₇	58/42	4600
P84	(EO) ₂₂ (PO) ₃₉ (EO) ₂₂	53/47	4200
P103	(EO) ₁₉ (PO) ₅₆ (EO) ₁₉	40/60	4900

cm⁻². The films were aged for at least 7 days at room temperature to reach equilibrium crystallinity.

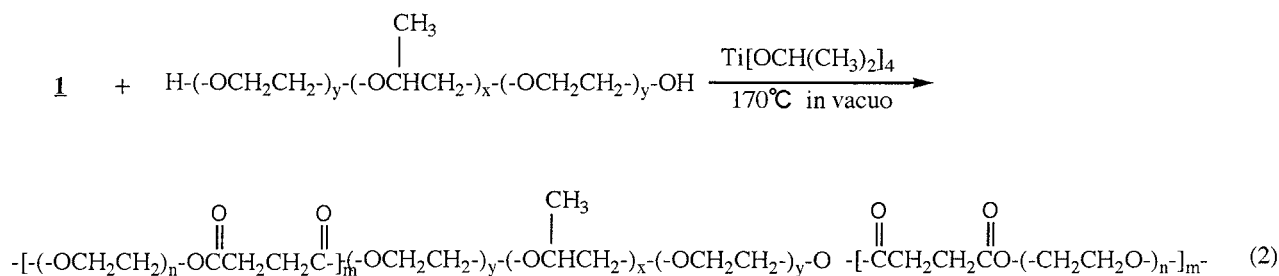
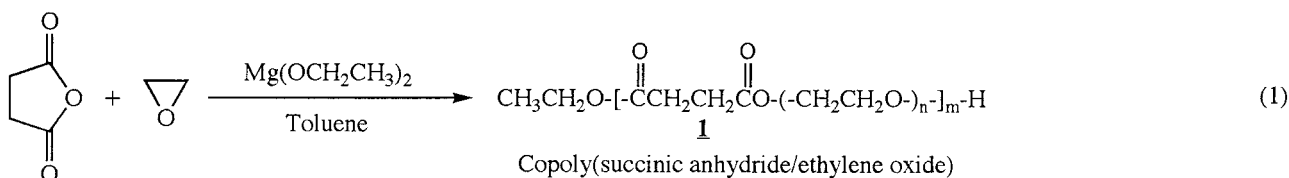
Analytical Procedures

¹H-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 tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier transform infrared spectrometer, by using film samples cast on a potassium bromide plate from chloroform solutions. DSC measurements were conducted with a Seiko Denshi DSC-120 for the sample from 4 to 8 mg, at a heating rate of 10°C min⁻¹ over a wide temperature range [from -60° to 120°C (first run)]. After the first run, the sample was cooled down to -60°C at a rate of about 10°C min⁻¹ and a

second run followed under the same conditions. *M_n* and molecular weight distributions (*M_w*/*M_n*) were determined with gel permeation chromatography (GPC) (TOSOH, HCL-8020). The columns were a TSKgel G4000HXL and a TSKgel G3000HXL, with a limited exclusion molecular weight of 4 × 10⁵. Chloroform was used as an eluent at a flow rate of 0.6 ml min⁻¹. Polystyrene standards with low polydispersities were used to generate a calibration curve. The residual titanium contents in the copolymers was analyzed according to JIS K0101 using a Shimadzu ICPS-1000 III sequential plasma spectrometer.

Enzymatic Degradation

Enzymatic hydrolysis tests were conducted as follows: 25 mg of polymer samples and 2 mL of phosphate buffer (KH₂PO₄/Na₂HPO₄, pH 7.0) were placed in a test tube, and the prescribed units of

**Scheme 1**

enzyme were added. Control tests were conducted for the polymers suspended without enzyme and for the enzyme itself. The enzyme used was the lipase from *Rhizopus arrhizus*. The enzymatic hydrolysis testings were conducted at 37°C for the fixed time. After filtration (0.2 μm membrane filter), total organic carbon (TOC) of the filtrate was measured with a TOC analyzer (Shimadu TOC 5000). The net TOC values were calculated by subtracting the average values at the two control tests from the average of two measurements.

Degradation by Activated Sludge

A schematic diagram of the apparatus for an aerobic degradation test has been presented in detail elsewhere.³⁸ 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 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:

$$\text{Biodegradation (\%)} = \left[\frac{\text{(Experimentally measured CO}_2\text{)}}{\text{(Theoretical CO}_2\text{)}} \right] \times 100$$

Theoretically released CO₂ was calculated from the composition determined from ¹H-NMR measurements of these copolymers by assuming that oligomers or monomers, first formed by enzymatic hydrolysis, were completely mineralized to CO₂.

RESULTS AND DISCUSSION

Polycondensation and Thermal Properties of Block Copolyesterethers

The results of the equimolar polycondensation of the copoly(SA/EO)s with PN of various M_n , and the kinds and the thermal properties of the ob-

tained copolymers are given in Table II. Table III shows the polycondensation results by varying the feed molar ratio of PN for copoly(SA/EO). The yields were higher than 70 wt %, except for the case of using relatively low M_n for copoly(SA/EO) (run 13 in Table II; run 7 and run 8 in Table III) and when high propylene oxide (PO) contents of PN was used. The low yield is due to the higher solubility of the copolymer containing long-chain length of polyoxypropylene (PPO) moiety in petroleum ether used as a precipitant at the work-up step. ¹H-NMR spectra of the obtained copolymer showed the proton signal (*s*, δ = 1.5–1.8 ppm) of the carboxylic or hydroxy group at the end of the polymers, except for the proton signals in the two prepolymers (—SA—, *s*, δ = 2.65 ppm, —SA—EO—SA—, *s*, δ = 4.33 ppm, —EO—SA—, *s*, δ = 4.25 ppm, —EO—PO—, *s*, δ = 3.7 ppm, —EO—EO—EO—, *s*, δ = 3.65 ppm, —EO—PO—, *m*, δ = 3.4–3.6 ppm, —PO—, *m*, δ = 1.15 ppm). The DSC curves showed two endotherm peaks attributed to the copoly(SA/EO) and the polyoxyethylene (PEO) segment in PN. In addition, GPC curves of the copolymers showed unimodal peaks. These results indicate that the obtained polymers are block copolyesterethers. The SA content of the block copolymers synthesized by polycondensation of equimolar prepolymers was higher than the one calculated from the feed molar ratio of the prepolymers. On the other hand, PO content in their block copolymers was much smaller than that calculated from the feed molar ratio of the prepolymers. PO content in the copolymers was shown to undergo a significant drop, with an increase in the M_n of the copoly(SA/EO). On the contrary, the composition, SA/EO/PO, was nearly equal to the calculated one from the prepolymers feed molar ratio, with an increase in the ratio of PN for copoly(SA/EO) (run 1–run 4 in Table III). Their respective M_n s were found to be higher than 170,000 and their polydispersities have risen above 3.7 (run 3 and run 4 in Table III). These results suggest that the polycondensation of copoly(SA/EO) or PN itself take place in addition to the reaction between copoly(SA/EO) and PN, and the obtained copolymers are multiblock copolymers.

Using the copoly(SA/EO) with $M_n = 2,400$, PO contents in the block copolymer were higher than the calculated ones (run 12 and run 13 in Table II). The molecular weight distributions (M_w/M_n) of the block copolymers, synthesized by equimolar polycondensation, were nearly equal to those of

Table II Yield, Structural Characterization, Thermal Properties (T_m , T_g , ΔH) and Biodegradability (TOC) of Copolymers, Synthesized by Equimolar Polycondensation of Copoly[succinic anhydride (SA)/ethylene oxide (EO)] with Pluronic^a (PN)

Run	Copoly (SA/EO)		PN		Unit Ratio in Feed		Unit Ratio ^b		Block Copolymer					
	Comp. ^b SA/EO (mol %)	$M_n^c/10^4$	Comp. EO/PO (mol %)	$M_n/10^4$	SA/EO/PO (mol %)	Yield (%)	SA/EO/PO (mol %)	Yield (%)	$M_n^c/10^4$	M_w/M_n^c	T_m^d (°C)	ΔH^d (J/g)	T_g^e (°C)	T_c^e (°C)
1	48/52	2.1	83/17	0.84	24/67/9	83	34/60/6	7.3	2.0	33, 94	8, 47	-41	-7, 40	10
2	48/52	2.1	58/42	0.46	24/55/21	80	24/56/10	8.2	1.9	13, 92	2, 46	-14, -42	37, 75	10
3	48/52	2.1	53/47	0.42	24/52/24	81	31/48/11	8.6	1.8	93	42	-14, -45	43	5
4	48/52	2.1	51/49	0.22	24/51/25	77	40/51/9	4.6	2.1	94	28	-19	59	10
5	48/52	2.1	40/60	0.49	24/46/30	74	32/59/9	6.8	2.0	93	50	-14	56	5
6	48/52	2.1	17/83	0.45	24/34/42	84	45/40/15	5.9	2.0	94	50	-14	56	20
7	48/52	2.1	17/83	0.20	24/34/42	86	34/52/14	6.0	1.6	95	20	-13, -45	43	30
8	48/52	2.1	20/80	0.11	24/36/40	87	37/55/8	6.7	2.0	93	26	-18	46	260
9	48/52	0.81	83/17	0.84	24/67/9	81	19/72/9	8.9	1.9	46, 96	13, 10	-45	-18, 26	150
10	48/52	0.81	53/47	0.42	24/52/24	76	36/46/18	4.6	2.1	21, 96	1, 15	-15	33, 73	150
11	48/52	0.81	17/83	0.45	24/34/42	61	43/48/9	4.1	2.2	96	59	-14	33, 75	160
12	49/51	0.24	83/17	0.84	24/67/9	98	7/79/14	11.8	1.5	47, 79	64, 5	-42	—	110
13	49/51	0.24	53/47	0.42	24/52/24	43	14/44/41	8.5	1.9	14, 87	9, 14	-45	—	160

^a Triblock [poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene)].

^b Determined by ¹H-NMR.

^c Determined by GPC.

^d Determined by DSC (first run).

^e Determined by DSC (second run).

^f The total organic carbon based on the water-soluble compounds produced by enzymatic hydrolysis using the lipase (500U) from *Rhizopus arrhizus*.

Table III Yield, Structural Characterization, Thermal Properties (T_m , T_g , ΔH) and Biodegradability (TOC) of Copolymers, Synthesized by Polycondensation of Copoly(SA/EO) with PN^a

Run	Copoly(SA/EO)		PN		Feed		Block Copolymer								
	Comp. ^b SA/EO (mol %)	$M_n \times 10^{-4}$	Comp. EO/PO (mol %)	$M_n \times 10^{-4}$	Copoly (SA/EO)/PN (mol %)	Unit Ratio SA/EO/PO (mol %)	Yield (%)	Unit Ratio SA/EO/PO (mol %)	$M_n \times 10^4$	M_w/M_n^c	T_m^d (°C)	ΔH^d (J/g)	T_g^e (°C)	T_g^e (°C)	TOC ^f (ppm)
1	48/52	2.4	83/17	0.84	75/25	36/60/4	90	33/64/3	6.5	2.1	35, 98	1, 48	-13	36, 76	0
2	48/52	2.4	83/17	0.84	49/51	24/67/9	91	31/64/5	5.8	3.2	37, 95	32, 44	-40	31, 76	50
3	48/52	2.4	83/17	0.84	26/74	12/75/13	83	19/72/9	17.5	4.1	36, 94	31, 37	-41	11, 37	200
4	48/52	2.4	83/17	0.84	10/90	5/80/15	82	8/77/15	17.3	3.7	44	50, 7	—	—	950
5	48/52	0.81	53/47	0.42	75/25	35/53/12	88	32/58/10	4.4	2.0	97	57	-17	32, 74	90
6	48/52	0.81	53/47	0.42	50/50	24/52/24	76	36/46/18	4.6	2.1	21, 96	2, 53	-15	33, 73	150
7	49/51	0.24	53/47	0.42	75/25	35/53/12	51	25/52/23	4.6	2.2	19, 94	3, 36	-65, -17	54	10
8	49/51	0.24	53/47	0.42	50/50	24/52/24	43	14/44/41	8.5	1.9	14, 87	9, 14	-45	—	160

^a Triblock [poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene)].

^b Determined by ¹H-NMR.

^c Determined by GPC.

^d Determined by DSC (first run).

^e Determined by DSC (second run).

^f The total organic carbon based on the water-soluble compounds produced by enzymatic hydrolysis using the lipase (500 U) from *Rhizopus arrhizus*.

copoly(SA/EO)s. This fact indicates that the segments of the copoly(SA/EO)s are hardly decomposed under the polycondensation conditions. As previously described, the DSC curves of the block copolymer including the long EO segment in the PN (F_{68} , $M_n = 8,350$, PO/EO = 17/83 mol %) showed two endotherm peaks due to fusion of crystals consisting of the copoly(SA/EO) segment and the PEO segment. The T_m of the block copolymers (from 93°C to 97°C) slightly changed, compared with that of the copoly(SA/EO). The T_m s of the polymers containing PEO depended on the EO length and the M_n s of copoly(SA/EO)s, and varied from 13°C to 47°C. In the case of using PN with PO content higher than 70 mol %, the T_m due to the PEO segments were not observed. The fusion heat (ΔH) of the block copolymers increased with the increase in the M_n s of copoly(SA/EO)s and the EO content in the PN. The T_g s of the block copolymers, including the longer PEO segments, were observed at two temperatures: one was due to the copoly(SA/EO) at -13°C up to -18°C and another attributed to the PN at -40°C to -45°C (run 2, run 3, and run 7 in Table II). No T_g s for the block copolymers consisting of short segments of copoly(SA/EO) and of PN were observed (e.g., run 9, run 12, and run 12 in Table II). The recrystallization peak (T_c) from the second-run DSC curves was observed, except for using low M_n copoly(SA/EO) or the PN, including the larger PO content. The DSC curves of the block copolymers containing the longer EO segments showed two recrystallization peaks. It became apparent that either a decrease in the M_n of copoly(SA/EO) or an increase in PO content resulted in lower recrystallization rates.

Therefore, the polycondensation of copoly(SA/EO) with PN and the morphology of the obtained block copolyesterethers could be characterized as follows: the PO content in the block copolymers increased, compared with that calculated from the feed ratio with a decrease in the M_n of copoly(SA/EO). The polycondensation of copoly(SA/EO) with PN proceeded faster, with lower M_n copoly(SA/EO) and at high molar feed ratio of PN to copoly(SA/EO). Thus, multiblock copolymers of a high M_n were produced. The copoly(SA/EO)s of composition, SA/EO = 48/52 or 49/51 mol %, were semicrystalline⁴¹ (the degree of crystallinity was about 30 wt %, from wide-angle X-ray diffraction). On the other hand, the EO segments in the used PN were within an M_n range from 80 to 3,000, and the PPO segment was within an M_n range from 950 to 3,800. The PN has a crystalline

PEO segment containing various lengths of a non-crystalline PPO segment as a center block segment. Therefore, the composition and M_n of both prepolymers may greatly influence the higher order structure of the obtained block copolymers. The T_m and the ΔH of block copolymers were approximately equal to that obtained when copoly(SA/EO) was used as a prepolymer apart from the block copolymers containing the copoly(SA/EO) of $M_n = 2,400$. The crystallization behavior of the copoly(SA/EO) segment in the block copolymer hardly changed by the polycondensation with PN. Furthermore, the T_g of the block copolymers was observed at the same temperature as that of the prepolymer copoly(SA/EO). These results suggest that the block copolymers have a microphase separation structure between the higher M_n copoly(SA/EO) and PN. However, the presence of this type of morphology is not supported by microscopic observations or small-angle X-ray scattering measurements. On the other hand, the PO content in the block copolymer, including the copoly(SA/EO) with $M_n = 2,400$, was higher than calculated by the prepolymer initial feed and composition. The SA content in the final block copolymer decreased, compared with that in the feed molar ratio. In addition, the T_m of the block copolymers and the ΔH based on copoly(SA/EO) segment fell and no T_c was observed. Therefore, it is apparent that the low M_n copoly(SA/EO) is partly decomposed though polycondensation under the previously described conditions, and the block copolymer is the product of recombination of the decomposed copoly(SA/EO) with PN, or it is produced by an introduction of PN segment between the copoly(SA/EO) segments.

Enzymatic Degradation

Table II shows the results of the enzymatic degradation of the block copolymers, synthesized by the equimolar polycondensation reaction between the copoly(SA/EO) and various kinds of PN, by the lipase from *Rhizopus arrhizus*. Data on the block copolymers consisting of lower biodegradable copoly(SA/EO) (i.e., $M_n = 21,000$, SA/EO = 48/52 mol %) and various kinds of PN are given in Table II (run 1 to run 8). These block copolyesterethers (run 1 to run 8) exhibited a microphase separation structure as previously described. In general, the characteristics of a polymer with a microphase separation structure depend on those of their components. In such case, both prepolymers are hardly enzymatically degraded.

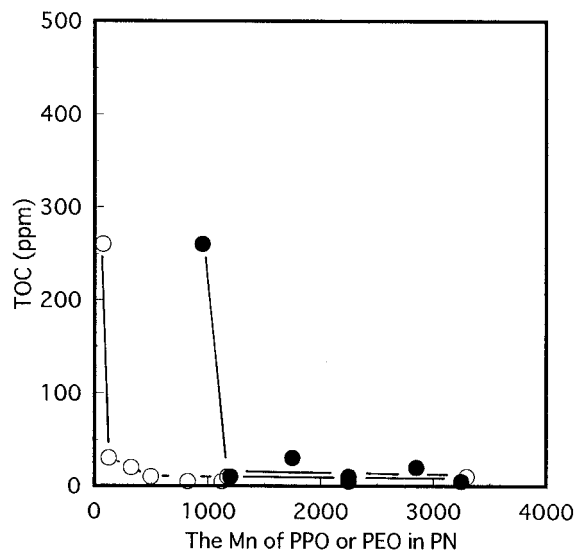


Figure 1 Degradability of the block copolyesterethers versus the M_n of polyoxypropylene, PPO (●) or polyoxyethylene, PEO (○) in Pluronic™, PN.

Figure 1 shows the relationships between the M_n of PEO or PPO in PN moiety and the enzymatic degradability of the obtained block copolymers. It is apparent that the biodegradability of the obtained block copolymers drastically decreased when the M_n of PPO or PEO in PN is higher than 1,000 or 125, respectively. However, these results are not compatible with those obtained by using PEO or PPO independently, whereas the biodegradability of the copoly(SA/EO) containing homo-PEO sequence was enhanced at high EO content.³⁸ Therefore, it is necessary to take into account the combined actions of both PEO and PPO segments, in PN moiety, on the biodegradation behavior of the block copolymers. In the polycondensation between the different M_n of copoly(SA/EO) and the PN(P84), the block copolymers using the copoly(SA/EO), $M_n = 8,100$ (run 10) or $M_n = 2,400$ (run 13), were shown to be enzymatically degradable, whereas the block copolymers [copoly(SA/EO) of $M_n = 21,000$ (run 3)] were hardly biodegradable.

The enzymatic degradabilities of the block copolymers obtained through polycondensation by changing the feed molar ratio of PN to copoly(SA/EO), are summarized in Table III. The enzymatic degradability of these copolymers increased considerably, with an increase in the ratio of PN in feed (run 1 to run 4). It is noteworthy that, in the case of run 4, the biodegradability could not be correctly evaluated because the TOC value of the blank test was extremely high due to the high

solubility of the copolymer in the phosphate buffer solution. The overall enzymatic behavior of these polymers in terms of their morphology could be summarized as follows: 1) the enzymatic degradabilities of the block copolymers with a microphase separation structure are strongly affected by the inherent degradability of their own prepolymers; 2) the block copolymers synthesized by using the low M_n prepolymers [copoly(SA/EO) and PN] were enzymatically degradable, because the PN segments were compatible with the copoly(SA/EO) segments without a microphase separation structure; 3) the block copolymers, containing PPO of M_n higher than 1,000, have a microphase separation structure and are endowed with low biodegradabilities; and 4) the ΔH_s of the block copolymers, an expression of crystallinity, are depressed with an increase in PN in feed, whereas the enzymatic degradability increases.

Degradation of Copolymers by Activated Sludge

Studies on biodegradation of typical block copolyesterethers, synthesized by polycondensation of copoly(SA/EO) with PN, were conducted using a standard activated sludge. Smulikaowska and Szpilowa⁴² reported that the biodegradation rate of the PNs by an activated sludge was heavily dependent on the PO content of the PNs. Figure 2 shows the results of the biodegradation estimated from the amount of the evolved CO_2 (IC measurement). The IC values resulted from the experimental values after subtracting the values for the control test, which was conducted in the absence of a copolymer. The block copolymer of feed composition, SA/EO/PO = 34/60/6 mol %, and of the $M_n = 73,000$ (run 1 in Table II) containing the PN(F68) [composition: EO/PO = 83/17 mol % and $M_n = 8,350$] was hardly biodegraded. The DSC curve for this block copolymer showed two endotherm peaks: one was attributed to the fusion of the copoly(SA/EO) segment and the other to the PEO segment. On the other hand, the copolymers of the composition SA/EO/PO = 45/40/15 mol % and of $M_n = 59,000$ (run 6 in Table II), synthesized using the PN[(L121) composition: EO/PO = 17/83 mol % and $M_n = 4,500$], was degraded by a standard activated sludge, and 60 wt % of the copolymer was converted into CO_2 for 28 days. The biodegradability of the block copolymer (composition: SA/EO/PO = 38/48/11 mol %, $M_n = 86,000$, run 3 in Table II) containing the PN[(P84) composition: EO/PO = 53/47 mol %] and was smaller than that of the block copolymer

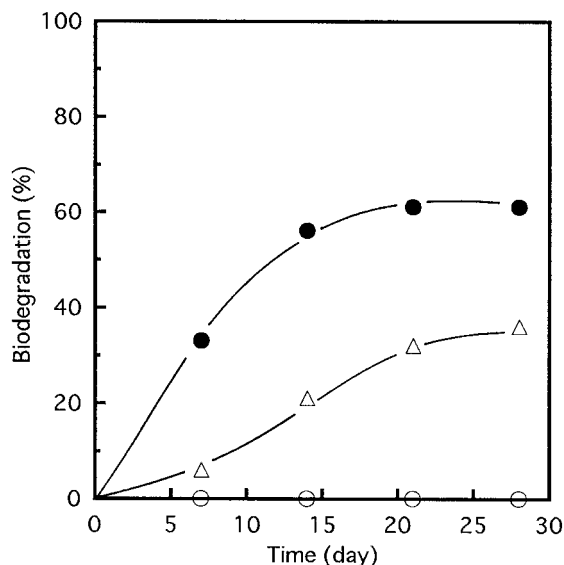


Figure 2 Biodegradation of typical block copolymers by a standard activated sludge at 30°C. (○) Block copolymer, SA/EO/PO = 34/60/6 mol %, $M_n = 73000$, synthesized from copoly(SA/EO) and PN(F68), EO/PO = 83/17 mol %, $M_n = 8350$. (●) Block copolymer, SA/EO/PO = 45/40/15 mol %, $M_n = 59000$, synthesized from copoly(SA/EO) and PN(L121), EO/PO = 17/83 mol %, $M_n = 4500$. (Δ) Block copolymer, SA/EO/PO = 41/48/11 mol %, $M_n = 86000$, synthesized from copoly(SA/EO) and PN(P84), EO/PO = 53/47 mol %, $M_n = 4200$.

(run 6 in Table II) containing the PN(L121; the M_n of PEO or PPO in L121 are 300, and 3,850, respectively). These results indicate that the biodegradation rates of the block copolymers by standard activated sludge substantially increased, with an increase in the PO content of the synthesized block copolymers and with an increase in the M_n of PPO segment in the PN moiety, in agreement with previously reported findings.⁴²

Ten milliliters of reaction mixture were taken up from the incubator in the biodegradation testing every week, filtered through 5A filter paper, and the TOC based on the water-soluble products in the filtrate was measured. Results are shown in Figure 3. The TOC value from the nondegradable copolymer (run 1 in Table II) was less than 10 ppm. On the other hand, those of biodegradable copolymers were around 30 ppm and remained constant throughout the testing period. This result strongly suggests that water-soluble products are not biodegraded by the activated sludge. These three-block copolymers were hardly degraded by the lipase from *Rhizopus arrhizus* (TOC values in Table II). However, these were

biodegraded by the activated sludge, except for the copolymers having a long PEO segment (run 1 in Table II). From these results, it is concluded that the biodegradation induced by lipase from *Rhizopus arrhizus* and the one caused by standard activated sludge follow a different path.

Polycondensation Without a Catalyst and Biodegradation

Polycondensation proceeded without a catalyst when the reaction temperature was raised from 170°C to 190°C. Results are shown in Table IV (run 1 and run 2). The value of M_w/M_n of the copolymer at run 1 was 2.6, and the T_g was observed at -28°C, clearly showing a shift to lower temperature, compared with the T_g of the prepolymer copoly(SA/EO) that was recorded at about -14°C. The solubility of the copolymer in the phosphate buffer solution was higher, compared with that of the polymer based on the prepolymer copoly(SA/EO). These results are in favor of the suggestion that the used prepolymer is first decomposed and later on reacts with the PN in the absence of a catalyst at 170°C for 19 h. The polycondensation rate increased proportionally to an increase in the EO content in the prepolymer copoly(SA/EO)s (run 2, run 3, and run 4). We previously reported that the number of hydroxy end groups of the copoly(SA/EO) increases with an increase in EO content of the copoly(SA/EO).³⁹ These experimental findings can be understood by the observed increase in the hydroxy end group of the copoly(SA/EO)s. The residual titanium content in the copolyesterether synthesized by TIP was around 390 ppm (run 5). The latter value was consistent with the one calculated from the concentration of the catalyst used. The effect of the residual titanium content on the biodegradation behavior was evaluated with the aid of biodegradation tests using a lipase or an activated sludge. The results are shown in Table IV and in Figure 4, respectively. It is apparent that the effect of the residual titanium content on the biodegradation behavior is unexpectedly negligible. However, the possibility of the polycondensation without a catalyst is a promising avenue to be further explored in view of the current environmental demand for lesser pollution of the environment. Introduction of PN as a prepolymer to the block copolymers is effective because of its high reactivity in the polycondensation and its ensuing biodegradability control. This dual function of PN should be attributed to the primary hydroxy end

Table IV Yield, Structural Characterization, Thermal Properties (T_m , T_g , ΔH) and Biodegradability (TOC) of Copolymers, Synthesized by Block Copolymerization of Copoly(SA/EO) with PN^a in the Absence of a Catalyst

Run	Copoly(SA/EO)		Feed			Block copolymer									
	Comp. SA/EO (mol %)	$M_n/10^4$	Copoly (SA/EO)/PN (mol %)	Unit Ratio SA/EO/PPO	Unit Ratio SA/EO/PPO (mol %)	Yield (%)	Time (h)	Temp. (°C)	Temp. (°C)	T_m^d (°C)	ΔH^d (J/g)	T_g^e (°C)	T_g^e (°C)	T_i^f (ppm)	TOC ^g (ppm)
1	48/52	0.93	40/60	20/68/12	13/77/10	91	19	170	170	48, 94	46, 19	-28	30	—	— ^h
2	48/52	0.93	40/60	20/68/12	13/77/10	87	6	190	190	42, 95	49, 26	-45	-24, 32	0	60
3	46/54	0.64	40/60	18/72/10	14/75/11	83	5	190	190	41, 84	56, 12	-46	-31	—	— ^h
4	38/62	0.88	38/62	17/71/12	10/80/10	76	3	190	190	43	66	-41	—	—	— ^h
5 ⁱ	48/52	1.17	42/58	20/70/10	16/75/9	82	6	170	170	45, 91	30, 25	-44	-18	390	160

^a Composition, EO/PO = 83/17 mol %, M_n = 8350.

^b Determined by ¹H-NMR.

^c Determined by GPC.

^d Determined by DSC (first run).

^e Determined by DSC (second run).

^f Residual titanium concentration in the copolymer after the polycondensation.

^g Total organic carbon of the water-soluble compounds produced by enzymatic hydrolysis using lipase (1000U) from *Rhizopus arrhizus* for 18 h at 37°C.

^h The exact TOC value could not be determined due to the higher solubility of the copolymer in the phosphate buffer solution.

ⁱ [Ti]OCH(CH₃)₂ was used as a catalyst for polycondensation.

groups and PPO segment, which influence the biodegradation behavior and the thermal properties of the novel copolymer by acting as a central block segment.

CONCLUSIONS

Thermal properties and 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 block copolyether, PN, were investigated, thus resulting in the following concluding remarks:

1. The block copolyesterethers synthesized by the polycondensation showed a microphase separation structure and maintained the thermal properties of their prepolymers.
2. The enzymatic degradabilities of the block copolymers depended on the compatibility of the both prepolymer segments.
3. The enzymatic degradabilities of the block co-

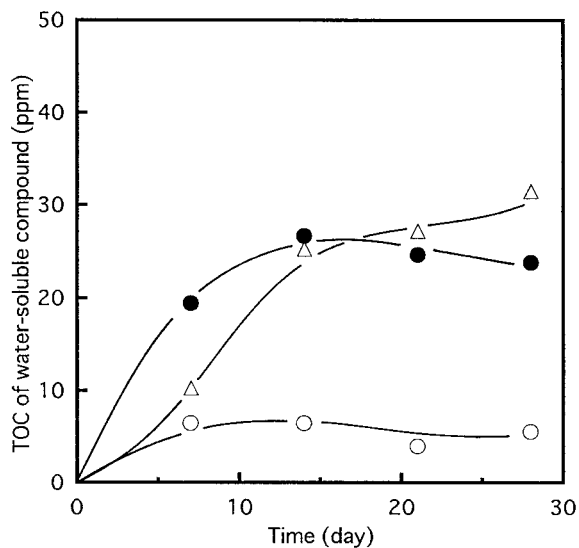


Figure 3 TOC of water-soluble compounds produced by a standard activated sludge (in the incubator for testing). (○) Block copolymer, SA/EO/PO = 34/60/6 mol %, $M_n = 73000$, synthesized from copoly(SA/EO) and PN(F68), EO/PO = 83/17 mol %, $M_n = 8350$. (●) Block copolymer, SA/EO/PO = 45/40/15 mol %, $M_n = 59000$, synthesized from copoly(SA/EO) and PN(L121), EO/PO = 17/83 mol %, $M_n = 4500$. (△) Block copolymer, SA/EO/PO = 41/48/11 mol %, $M_n = 86000$, synthesized from copoly(SA/EO) and PN(P84), EO/PO = 53/47 mol %, $M_n = 4200$.

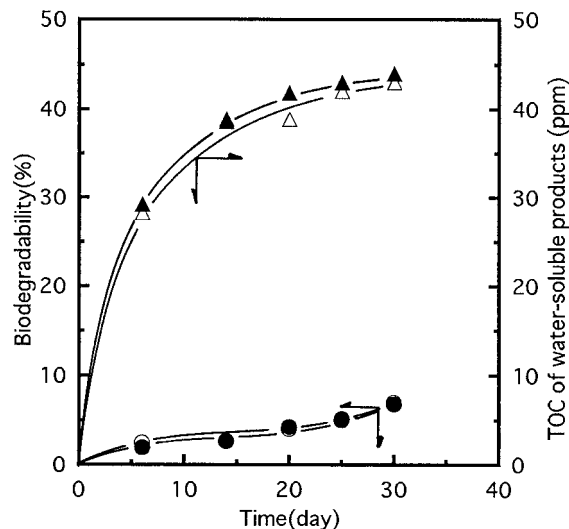


Figure 4 Biodegradation of block copolymers, synthesized with or without a catalyst, by a standard activated sludge at 30°C and TOC of water-soluble compounds produced by a standard activated sludge (in the incubator for testing). (○) Block copolymer, SA/EO/PO = 34/60/6 mol %, $M_n = 135000$, synthesized from copoly(SA/EO) and PN(F68), EO/PO = 83/17 mol %, $M_n = 8350$. Residual titanium content in the polymer was not observed. (●) Block copolymer, SA/EO/PO = 34/60/6 mol %, $M_n = 121000$, synthesized from copoly(SA/EO) and PN(F68), EO/PO = 83/17 mol %, $M_n = 8350$. Residual titanium content in the block copolymer was 390 ppm.

polymers decreased with an increase in PPO segment length of PN.

4. The biodegradation trends for the block copolymers by the lipase from *Rhizopus arrhizus* and the standard activated sludge were different.
5. The part of the water-soluble compounds produced by the biodegradation using the activated sludge remained in the reaction system without its conversion to CO_2 .
6. The polycondensations proceeded effectively without a catalyst at temperatures higher than 190°C.
7. The residual titanium in the block copolymers did not interfere with their biodegradation by activated sludge microbes.

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