

Comparison of Sm complexes with Sn compounds for syntheses of copolymers composed of lactide and cyclic carbonates and their biodegradabilities

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Abstract

The comparison of organolanthanide complexes, $(C_5Me_5)_2SmMe(THF)$ (Sm1) and $[(C_5Me_5)_2Sm]_2(PhC=C=C=CPh)$ (Sm2), with tin compounds, $Bu_2Sn(OMe)_2$ (Sn1) and $Bu_2Sn(OCH_2CH_2CH_2O)$ (Sn2), in the preparation of random, diblock, and triblock copolymers composed of L-lactide (L-LA) or D,L-LA and cyclic carbonates, trimethylene carbonate (TMC) or 2,2-dimethyltrimethylene carbonate (DTC) is reported. The biodegradabilities of the resulting copolymers with proteinase K and a compost were examined. The copolymerization of L-LA with cyclic carbonates by Sm1 or Sm2 afforded copolymers with relatively low melting points ($<160\text{ }^\circ\text{C}$) due to the accompanying epimerization in comparison with those obtained with Sn1 or Sn2. In the degradation of the polymers with a compost, the copolymers based on D,L-LA were more degradable than those based on L-LA. On the other hand, the effect of the incorporated cyclic carbonate on its degradability was more drastic in the copolymers based on L-LA than those in the copolymers based on D,L-LA. The introduction of only a small amount of the cyclic carbonates into PLLA significantly enhanced the degradability of PLLA with a compost or proteinase K. In the enzymatic degradation of L-LA-containing polymers, the copolymerization of L-LA with TMC was also quite effective to improve the degradability of PLLA. Triblock copolymerization tends to be effective to enhance the degradability of PLLA.

Keywords: Copolymer; Lactide; Cyclic carbonate; Enzymatic degradation; Compost degradation

1. Introduction

Poly(L-lactide) (PLLA), produced at industrial scale from starch by Cargill-Dow, is one of the most promising biocompatible and biodegradable semicrystalline polymers [1–5]. PLLA has been widely studied for biomedical applications, particularly those that demand good mechanical properties for surgical sutures and devices for internal bone fixation [6–10]. However, homopoly(L-LA) has been reported to exhibit relatively poor biodegradability. Furthermore, PLLA is too hard and too brittle to be used as general purpose biodegradable materials. Thus, physical properties should be improved by copolymerizations of lactide with other monomers in order to generate softer and tougher materials. For this purpose, cyclic carbonates are of great interest as comonomers because of the soft property of the resulting copolymers [11–17]. In our previous works, we studied synthesis and biodegradabilities of random copolymers of L-LA with (*R*)-, (*S*)-, or *rac*-1-methyltrimethylene carbonate polymerized by using a samarium initiator $(C_5Me_5)_2SmMe(THF)$ (Sm1) [18–23]. We have also reported random, diblock, and triblock copolymers of L- and D,L-LA with achiral cyclic carbonates such as trimethylene carbonate (TMC) and 2,2-dimethyltrimethylene carbonate (DTC) polymerized by using Sm1 or a bifunctional initiator $(C_5Me_5)_2Sm(PhC=C=C=CPh)Sm(C_5Me_5)_2$ (Sm2) [24,25]. On the other hand, high molecular weight poly(LA)s were prepared using tin compounds such as $Sn(2\text{-ethylhexanoate})_2$ and $Bu_2Sn(OR)_2$ [5,15,26–31]. This paper describes the comparison of the activities between Sm complexes and Sn compounds for random and diblock copolymerization of LA and cyclic carbonates together with the triblock copolymerization, and their biodegradabilities with a compost and with proteinase K.

2. Experimental

2.1. General

^1H NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (400MHz). Chemical shifts were calibrated using CHCl_3 in CDCl_3 at 7.26 ppm. Number average molecular weights and molecular weight distributions of copolymers were determined by gel permeation chromatography (GPC) on a Tosoh SC-8010 high speed liquid chromatograph equipped with a differential refractometer, using CHCl_3 as an eluent at 40 °C (flow rate, 1.0 ml). The columns used were TSK gel G5000_h, G4000_h, G3000_h, and G2000_h. Molecular weights were determined by using a universal curve plotted with narrow-polydispersity polystyrene standards, whose M_w values were determined by a light-scattering method. T_g and T_m values were measured on a Seiko SSC-5100 DSC-22C apparatus. The polymer samples were scanned from -100 to 120 °C at a heating rate of 10°C min⁻¹ under nitrogen stream. T_m and $-\Delta H_m$ (heat of fusion) values were determined in the first heating, while the T_g in the second heating.

2.2. Materials

Tetrahydrofuran and toluene were dried over CaH_2 for 5 days, then over Na metal for 10 days and distilled before use. Commercially available L-lactide and D,L-lactide (Aldrich) were dissolved in THF, dried over CaH_2 for 10 days and sublimed twice before use at 110°C. Trimethylene carbonate (TMC) and 2,2-dimethyltrimethylene carbonate (DTC) were gifted from Daicel Co. and purified by distillation in vacuo. $(\text{C}_5\text{Me}_5)_2\text{SmMe}(\text{THF})$ [32] (Sm1), $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\text{PhC}=\text{C}=\text{C}=\text{Ph})$ [33] (Sm2) and $\text{Bu}_2\text{Sn}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{O})$ (Sn2) [34] were prepared according to the known methods. The enzyme, proteinase K (*Tritirachium album*, activity 20 IU/mg, Wako Pure Chemical), in Tricine buffer, *N*-[tris(hydroxymethyl)methyl]glycine, at pH 8.0, was used without further purification. Ion exchanged water was used for biodegradation tests.

2.3. Block copolymerizations of lactide with cyclic carbonates by samarium initiators

A typical procedure: TMC (0.11 g, 1.07 mmol) was first treated with $(\text{C}_5\text{Me}_5)_2\text{SmMe}(\text{THF})$ (Sm1, 21.5 μmol) in toluene at 110 °C for 1 h, and then L-LA (1.34g, 9.69mmol) was successively added to the mixture followed by heating to 130 °C for 23 h. The resulting mixture was poured into 100 mL of methanol in order to precipitate the resulting copolymer. The precipitates were dissolved in chloroform and then added again to excess methanol to reprecipitate the copolymer. 51% yield. The TMC/L-LA ratio in the copolymer was 91/9mol/mol as analyzed by ^1H NMR. In a similar manner, diblock copolymers of LA with DTC were performed by the addition of DTC to the initiator followed by stirring at 120 °C for 1 h in toluene, and then L-LA was added to the mixture followed by stirring at 120°C for 23h. PLLA-*b*-PTMC: ^1H NMR (400 MHz, CDCl_3) δ 1.58 (m, CH_3 -LA), 2.05 (m, 2- CH_2 -TMC), 4.24 (t, OCH_2 -TMC), 5.16 (q, OCH-LA). PLLA-*b*-PDTC: ^1H NMR (400 MHz, CDCl_3) δ 1.00 (s, CH_3 -DTC), 1.58 (m, CH_3 -LA), 3.97 (s, OCH_2 -DTC), 5.16 (q, OCH-LA). PDLLA-*b*-PTMC: ^1H NMR (400 MHz, CDCl_3) δ 1.57 (m, CH_3 -LA), 2.05 (m, 2- CH_2 -TMC), 4.24 (t, OCH_2 -TMC), 5.17 (m, OCH-LA). PDLLA-*b*-PDTC: ^1H NMR (400 MHz, CDCl_3) δ 1.00 (s, CH_3 -DTC), 1.58 (m, CH_3 -LA), 3.97 (s, OCH_2 -DTC), 5.17 (m, OCH-LA).

Sequential copolymerization of L-LA (1.31 g, 8.9mmol) with TMC (0.1 g, 0.9mmol) was carried out using $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\text{PhC}=\text{C}=\text{C}=\text{Ph})$ (Sm2, 19.6 μmol) as an initiator. First TMC was added to the toluene solution of the initiator and stirred for 3 h at ambient temperature, and then L-LA was added to the mixture followed by heating to 80 °C for 12h. The reaction mixture was poured into 100 mL of methanol to precipitate the resulting triblock copolymer. The precipitates were dissolved in chloroform and then added again to excess methanol to reprecipitate the copolymer. The yield was 84%.

2.4. Block copolymerizations of lactide with cyclic carbonates by tin initiators

Diblock copolymers were prepared by sequential copolymerization of TMC (1.65 g, 16.2mmol) and L-LA (21.35 g, 148mmol) by using $\text{Bu}_2\text{Sn}(\text{OMe})_2$ (Sn1, 0.25 mmol) as an initiator. First TMC was added to the initiator in solution in 5 ml of toluene in a glass reactor and stirred for 16 h at 80 °C, and then this solution is transferred to a second glass reactor containing L-LA and 25 ml of toluene. The polymerization was then stirred at 80 °C for 7 h. An excess of HCl 1 N was added to the polymerization mixture, which was then poured into 100 mL of methanol to precipitate the resulting diblock copolymer. The yield was 95%.

Triblock copolymers were prepared by sequential copolymerization of TMC (1.48 g, 14.5 mmol) and L-LA (20.85g, 145mmol) by using $\text{Bu}_2\text{Sn}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{O})$ (Sn2, 0.375 mmol) as an initiator. First TMC was added of the initiator in solution in 5 ml of toluene in a glass reactor and stirred for 16 h at 80 °C, and then this solution is transferred to a second glass reactor containing L-LA and 25 ml of toluene. The polymerization was then stirred

at 80 °C for 7 h. An excess of HCl 1 N was added to the polymerization mixture, which was then poured into 100mL of methanol to precipitate the resulting triblock copolymer. The yield was 95%.

2.5. Degradation by a compost

Commercially available effective microorganism (EM) fermented solution (30 ml) containing *Rho-dospirillum*, *Rhodopseudomonas*, *Pseudomonas*, *Micrococcus*, *Bacillus*, *Lactobacillus*, *Streptococcus*, *Saccharomyces*, *Aspergillus*, *Penicillium* etc. and theriaca syrup (40 ml) were added to 2000 ml of water, and this solution was sprayed on the mixture of rice hulls (5 kg) and rice bran (15 kg). Resulting material was wrapped with a polyethylene film and then dried in the shade for 1 day. The content of water was evaluated by the weight loss of the samples after heating them to 200 °C. The samples were sealed in polyethylene mesh and it was hold in the resulting compost for a fixed time. The evaluation of the biodegradation was carried out by measuring the weight loss with a compost.

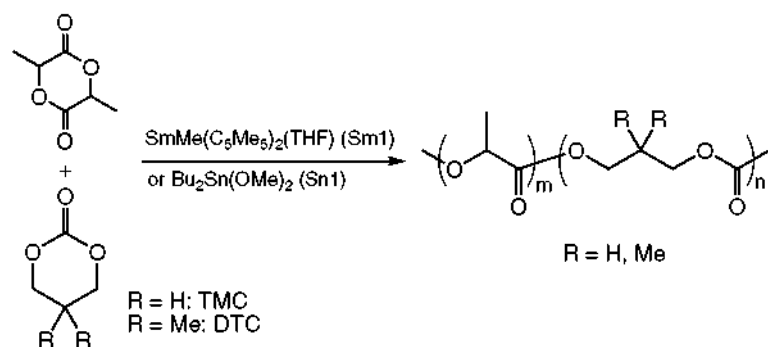
2.6. Enzymatic degradation

Enzymatic degradations of copolymers by proteinase K were carried out in Tricine buffer (pH 8.0) by exposing the polymer samples in the solution followed by determining the weight loss gravimetrically after recovering the samples at intervals. The used polymer films were prepared by the solvent casting method. The size and weight of the films used were 5 x 5 mm (thickness 50-70 μm) and 10– 15mg, respectively. Three samples were used to obtain one data and the averaged value was used (standard deviation, ±4%). The enzyme and the buffer solution were replaced every 24 h so that the enzyme activities maintain at a desired level throughout the experiment. The bottle (50 ml volume) containing a sample, an enzyme and the buffer solution were warmed to 37 °C with stirring. After a fixed time, the samples were removed from the bottle, washed with 99.5% ethanol and then dried to constant weight (5 h) in vacuo before weighing.

3. Results

3.1. Synthesis of copolymers composed of L- or D, L-lactide and cyclic carbonates

Random and diblock copolymerizations of L- or D,L-LA with cyclic carbonates were demonstrated in toluene using $(C_5Me_5)_2SmMe(THF)$ (Sm1) or $Bu_2Sn(OMe)_2$ (Sn1) as an initiator (Scheme 1). The representative results are summarized in Table 1. Block copolymerizations were performed by reacting first cyclic carbonate at 110 or 80°C using Sm1 or Sn1, respectively, and then L-LA or D,L-LA was added to the resulting polymer complex at 110°C (Scheme 1). Reversed addition did not produce the desired copolymer and afforded mainly poly(LA). A bifunctional binuclear samarium complex, $(C_5Me_5)_2Sm(PhC=C=C=CPh)Sm(C_5Me_5)_2$ (Sm2), was reported to polymerize ε-caprolactone to form bifunctional polymers [35].



Scheme 1.

We used the complex Sm2 to the synthesis of triblock copolymer of lactide and cyclic carbonates to afford a new functionalized polymer material (Scheme 2). Triblock copolymerizations of LA/cyclic carbonates/LA also take place using an unique bifunctional tin initiator, $Bu_2Sn(OCH_2CH_2CH_2O)$ (Sn2, Scheme 3) [36]. Cyclic carbonate was first added to the initiator Sm2 or Sn2, and then L-LA or D,L-LA was reacted. Reversed addition again did not produce the desired copolymer and afforded homopoly(LA). The results are also included in Table 1. We prepared copolymers with high LA-content (~90%) in this study, because we have proved only a small incorporation of cyclic carbonates significantly improve the degradability of PLA-based copolymers [24]. Sm1 initiated polymerizations gave polymers in relatively low yield compared with the Sn1 initiated polymerizations,

but the M_n s are high and M_w/M_n s are rather low.

Throughout this paper, we applied a five digit abbreviation system to indicate copolymers, in which the first digit represent the copolymerization mode (R, random; D, diblock; T, triblock), the second digit the kind of lactide (L, L-LA; R, D,L-LA (meaning racemic)), the third digit the kind of cyclic carbonates (T, TMC; D, DTC), and the last two digits the LA content (mol%) of the copolymer. Each polymer abbreviation is followed by the used initiator (Sm1, Sn1, Sm2, or Sn2).

Block copolymers containing L-LA were semicrystalline and showed melting point from PLLA segments. The melting points of the L-LA-containing polymers obtained with Sm initiators were lower than 160 °C, indicating the lower crystallinity of the polymers due to accompanying epimerization.

Table 1 Copolymerization of L-LA or D,L-LA with cyclic carbonated using Sm1, Sm2, Sn1, and Sn2 compounds^a

Polymer	LA fraction (mol%)		Yield %	$M_n \cdot 10^4$	M_w/M_n	T_m °C	$-\Delta H_m$ (J/g)	T_g °C
	Feed	Found						
PLLA-co-PTMC								
RLT97-Sm1	90	97	58	8.5	1.4	156	30	49
RLT91-Sn1	90	91	95	1.8	1.7	–	–	23
DLT81-Sm1	90	81	51	7.0	1.7	158	36	–18, 55
DLT91-Sn1	90	91	95	6.8	1.3	171	45	53
TLT81-Sm2	90	81	84	8.8	1.7	153	55	20
TLT93-Sn2	91	93	95	6.7	1.4	173	40	58
PLLA-co-PDTC								
RLD95-Sm1	90	95	79	9.9	1.6	158	38	59
RLD93-Sn1	90	93	95	3.6	1.5	164	27	54
DLD94-Sm1	90	94	55	8.6	1.5	87,159	1.2,34	58,9
DLD94-Sn1	90	94	95	3.0	1.8	168	41	56
TLD83-Sm2	90	83	98	8.9	1.6	111,159	1.1,35	58
TLD93-Sn2	91	93	95	3.5	1.5	170	38	57
PDLLA-co-PTMC								
RRT87-Sm1	90	87	43	5.3	1.6	–	–	35
RRT91-Sn1	90	91	95	1.8	1.7	–	–	23
DRT79-Sm1	90	79	53	5.7	1.4	–	–	35
DRT93-Sn1	90	93	95	2.6	1.8	–	–	31
TRT83-Sm2	90	83	98	6.7	1.7	–	–	37
TRT92-Sn2	91	92	95	4.5	1.4	–	–	30
PDLLA-co-PDTC								
RRD87-Sm1	90	87	38	6.3	1.8	–	–	44
RRD92-Sn1	90	92	95	2.4	1.6	–	–	45
DRD92-Sm1	90	92	49	6.4	1.8	87	1	45
DRD93-Sn1	90	93	95	2.6	1.5	–	–	45
TRD84-Sm2	90	84	84	9.6	1.9	91	13	52
TRD93-Sn2	91	93	95	4.5	1.4	–	–	29

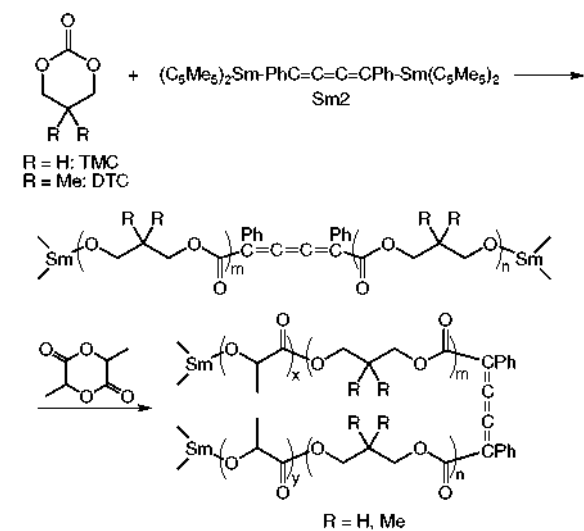
Sm1, SmMe(C₃Me₃)₂(THF) 0.2 mol% of monomer, Sn1, SnBu₂(OMe)₂ 0.2 ml% of monomer, Sm2, (C₃Me₃)₂(PhC=C=C=C=C(Ph))Sm(C₃Me₃)₂ 0.1 mol% of monomer, Sn2, SnBu₂(OCH₂CH₂CH₂O) 0.1ml% of monomer.

^a Reaction conditions, Sm1 system: 80 °C for 12 h in 4.0 ml toluene, Sn1 system: 110 °C for 12 h in 4.0 ml of toluene.

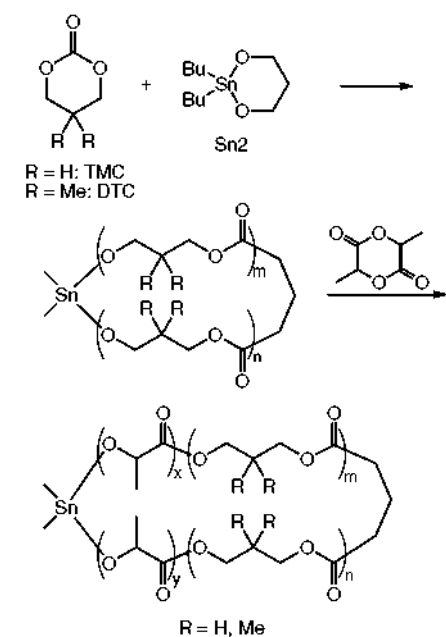
This has also supported by the lower negative value of optical rotation of PLLA produced by Sm1 than those of enantiopure PLLA [24]. The L-LA-containing diblock copolymers prepared by Sm1, DLT81-Sm1 and DLD94-Sm1, exhibit two glass transition points, while the corresponding triblock copolymers, TLT81-Sm2 and TLD83-Sm2, exhibited only one T_g . Thus, the triblock copolymers should have more homogeneous structure than the corresponding diblock copolymers. In contrast, the L-LA-containing polymers prepared by Sn initiators had higher melting points (>164°C). Random copolymers RLT97-Sm1, RLD95-Sm1, and RLD93-Sn1 showed melting points due to their high L-LA contents. Other L-LA-containing random copolymers were amorphous. All the D,L-LA containing copolymers were also amorphous.

3.2. Degradability of L-LA-Based copolymers by a compost

Degradation of lactide–cyclic carbonate copolymers were performed by a compost at 60°C. The biodegradabilities of random, diblock, and triblock PLLA-*co*-PTMC were summarized in Fig. 1.



Scheme 2.



Scheme 3.

Throughout this paper, circle, X, rhombus, square, and triangle plots represent homopoly(lactide), homopoly(cyclic carbonate), random copolymer, diblock copolymer, and triblock copolymer, respectively.

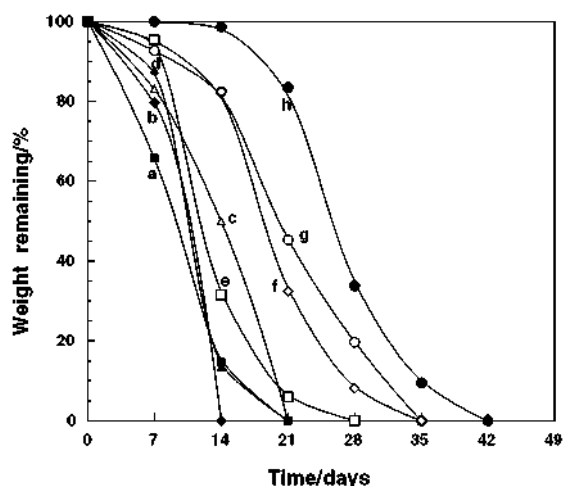


Fig. 1. Biodegradations of PLLA-co-PTMC by a compost at 60 °C. **a** DLT91-Sn1, **b** RLT91-Sn1, **c** TLT81-Sm2, **d** TLT93-Sn2, **e** DLT81-Sm1, **f** RLT97-Sm1, **g** PLLA-Sm1, **h** PLLA-Sn1.

For each plot, outline typeface means that the sample was prepared with Sm initiator, and filled typeface means that the sample was prepared with Sn initiator. Homo PLLA prepared by Sm1 (**g**) was more susceptible to compost degradation than that prepared by Sn1 (**h**), because of its lower crystallinity [25]. All the PLLA-co-PTMC copolymers showed higher degradability than these homo PLLAs. The random (**b**), diblock (**a**), and triblock (**d**) copolymers prepared by Sn initiators exhibited similar degradabilities, and the random copolymer was most degradable among them, completely degraded within 14 days. The copolymers prepared by Sm initiators (**c**, **e**, and **f**) tend to be less degradable than those obtained by Sn initiators. Although the reason is not clear, we speculate that the difference in LA contents or initiating end groups could affect their degradabilities. Among the samarium systems, the degradability is in an order of diblock ~ triblock > random. The low degradability of the random copolymer by Sm1 can be attributed the high L-LA content of this sample. The compost degradation of PLLA-co-PDTC is illustrated in Fig. 2. Homopoly(DTC) (**f**) was completely inert to compost degradation, and the PLLA-co-PDTCs are more degradable than both homopolymers PLLA and PDTC.

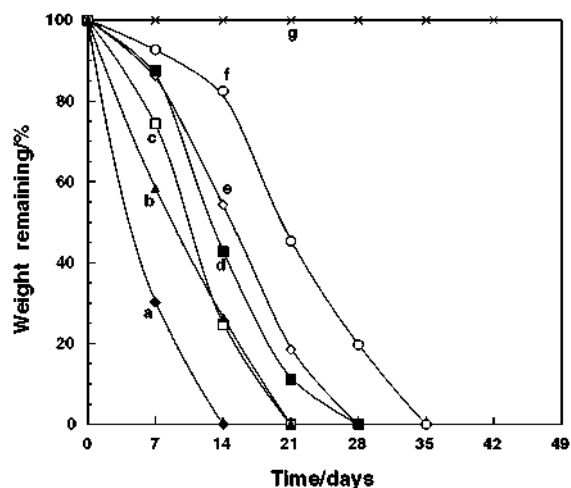


Fig. 2. Biodegradations of PLLA-co-PDTC by a compost at 60 °C. **a** RLD93-Sn1, **b** TLD83-Sm2, **c** DLD94-Sn1, **d** DLD91-Sm1, **e** RLD95-Sm1, **f** PLLA-Sm1, **g** PDTC-Sm1.

The PLLA-co-PDTCs were more degradable than the corresponding PLLA-co-PTMCs. The random copolymer prepared by Sn1 (**a**) showed the highest degradability among the tested samples as is the case of PLLA-co-PTMC. The copolymers prepared by Sn initiators again showed faster degradabilities than those prepared by Sm initiators. In comparison among the PLLA-co-PDTCs prepared by Sm initiators, triblock copolymer (**b**) was most degradable. RLD95-Sm1 (**e**) showed slow degradation in contrast to fast degradation of RLD93-Sn1 (**a**).

3.3. Degradability of D,L-LA-based copolymers by a compost

The results of compost degradation of PDLLA-*co*-PTMC are given in Fig. 3. Homo PDLLA (**c**) is significantly more susceptible to compost degradation than Homo PLLA (**h** in Fig. 1), and the PDLLA-*co*-PTMC also showed somewhat higher degradabilities than the corresponding PLLA-*co*-PTMCs, possibly due to the lower crystallinity of the D,L-LA based polymers. Among these copolymers, a triblock copolymer TRT83-Sm2 (**a**) was most degradable. On the other hand, the corresponding triblock copolymer prepared by Sn2 (**e**) was slightly less degradable than PDLLA.

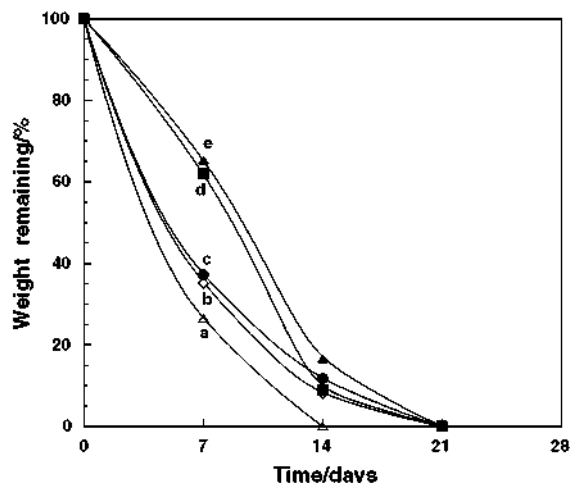


Fig. 3. Biodegradations of PDLLA-*co*-PTMC by a compost at 60 °C. **a** TRT83-Sm2, **b** RRT87-Sm1, **c** PDLLA-Sn1, **d** DRT93-Sn1, **e** TRT92-Sn1.

This difference could come from two times higher TMC content of the triblock copolymer prepared by Sm2 than that prepared by Sn2. The degradability of RRT87-Sm1 (**b**) was very similar to that of homo PDLLA.

Fig. 4 shows compost degradation of PDLLA-*co*-PDTc. The degradabilities of PDLLA-*co*-PDTc are also higher than those of the corresponding PLLA-*co*-PDTc, and similar to those of the PDLLA-*co*-PTMCs. It is notable that the PDLLA-*co*-PDTc prepared by Sm initiators (**a**, **b**, and **c**) are clearly more degradable than those prepared by Sn initiators (**e**, **f**, and **g**), especially, it is in sharp contrast in the degradability of the triblock copolymers prepared by Sm2 (**a**) and Sn2 (**g**). We speculate that this could come from lower LA content of the triblock copolymer prepared by Sm2. This difference could again be attributed to the higher TMC content of the copolymer prepared by Sm2 than that prepared by Sn2.

3.4. Enzymatic degradation of L-LA based copolymers with proteinase K

Enzymatic degradation of these polymers was performed by using Proteinase K in Tricine buffer (pH 8.0) at 37°C, and proceeded much more rapidly than the compost degradation. The results of enzymatic degradation of PLLA-*co*-PTMC are shown in Fig. 5.

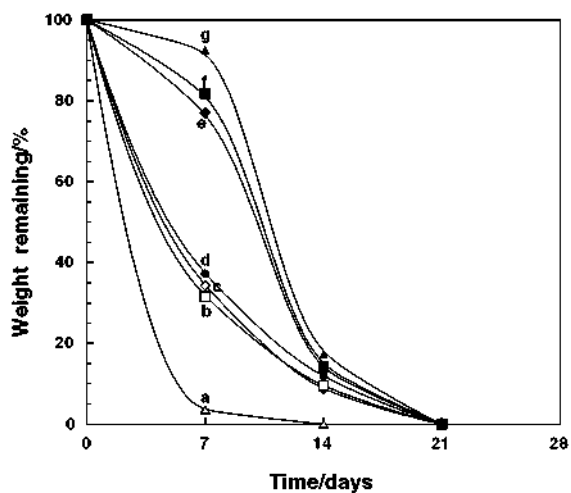


Fig. 4. Biodegradations of PDLLA-co-PDTC by a compost at 60 °C. **a** TRD84-Sm2, **b** DRD92-Sm1, **c** RRD87-Sm1, **d** PDLLA-Sn1, **e** RRD92-Sn1, **f** DRD93-Sn1, **g** TRD93-Sn2.

All the copolymers exhibited higher degradability than that of homo PLLA (**f**), and the triblock copolymer prepared by Sm2 (**a**) was most degradable among the PLLA-co-PTMCs examined here probably due to its suitable crystallinity. The random and diblock copolymers prepared by both Sm1 and Sn1 were also highly degradable.

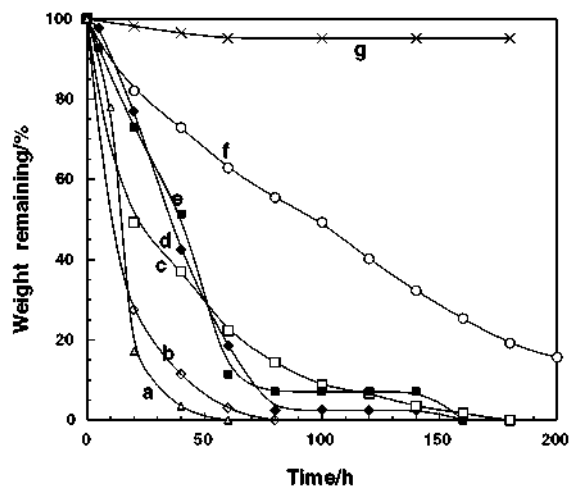


Fig. 5. Degradation of PLLA-co-PTMC by proteinase K at 37 °C. **a** TLT81-Sm2, **b** RLT71-Sm1, **c** DLT81-Sm1, **d** RLT91-Sn1, **e** DLT91-Sn1, **f** PLLA-Sm, **g** PTMC-Sm1.

In comparison with two random copolymers prepared by Sm1 and Sn1, the one prepared by Sm1 has apparently higher degradability than that of the other. This can be attributed to the lower crystallinity of the former caused by the accompanying epimerization. Although homopoly(TMC) (**g**) was only slightly degraded by Proteinase K, introduction of a small portion of PTMC segment dramatically improved degradability of PLLA. In some copolymer, the degradation slowed down when the remaining weight reached to ca. 10%, possibly due to low degradability of the PTMC segments.

3.5. Enzymatic degradation of D,L-LA based copolymers with proteinase K

Fig. 6 illustrates enzymatic degradation of PDLLA-co-PTMC. In sharp contrast to the case of PLLA-co-PTMC, a triblock copolymer prepared by Sn2, TRT92-Sn2 (**a**) showed good degradability. The degradability of RRT87-Sm1 (**b**) was similar to those of the triblock copolymer by Sn2 (**a**). The degradation of a triblock copolymer, TRT83-Sm2 (**d**) was rather slow probably due to its relatively low LA content.

Fig. 7 shows enzymatic degradation of PDLLA-co-PDTC. In this series, DRD92-Sm1 (**b**) was most degradable.

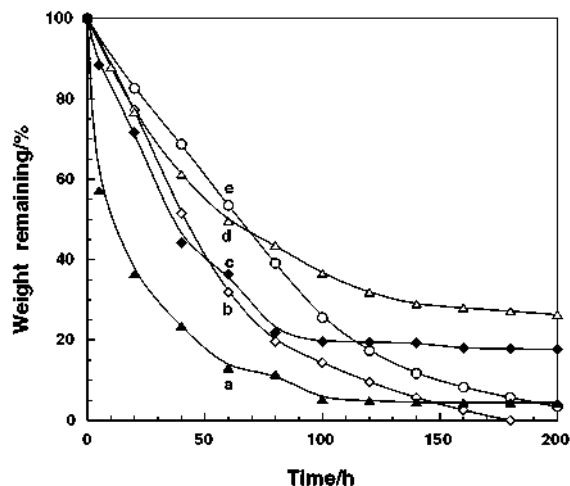


Fig. 6. Degradation of PDLLA-co-PTMC by proteinase K at 37 °C. **a** TRT92-Sn2, **b** RRT87-Sm1, **c** RRT91-Sn1, **d** TRT83-Sm2, **e** PDLLA-Sm1.

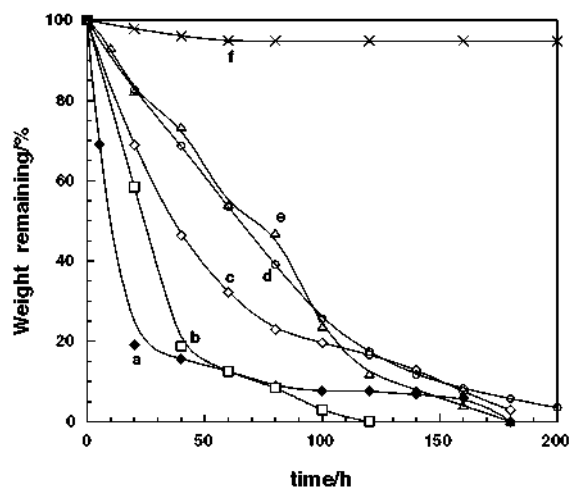


Fig. 7. Degradation of PDLLA-co-PDTC by proteinase K at 37 °C. **a** RRD92-Sn1, **b** DRD92-Sm1, **c** RRD87-Sm1, **d** PDLLA-Sm1, **e** TRD84-Sm2, **f** PDTC-Sm1.

RRD92-Sn1 (**a**) also showed similar degradability. The degradabilities of RRD91-Sm1 (**c**) and TRD84-Sm2 (**e**) were similar to that of PDLLA-Sm1 (**d**).

4. Discussion

In the random and block copolymerization of LA and cyclic carbonates, the Sn1 and Sn2 initiators tend to give higher polymer yields than the Sm1 and Sm2 complexes, probably due to high air- and moisture-sensitivity of the samarium compounds. The homo- and copolymerization of L-LA with cyclic carbonates by Sm1 or Sm2 afforded polymers with lower melting points (<160 °C) due to accompanying epimerization. The copolymerization modes, random, diblock, and triblock, could affect polymer morphology, e.g., the L-LA-containing diblock copolymers prepared by Sm1 exhibited two glass transition points, while the corresponding triblock copolymers exhibited only one T_g . This indicates that the diblock copolymer has micro phase separation, and that the triblock copolymer has more homogeneous structure.

In the degradation with a compost, PLLA-co-cyclic carbonates showed higher degradabilities than that of homopoly(L-LA). Random copolymerization of L-LA with cyclic carbonates by Sn1 was most effective to give highly degradable copolymers. In the compost degradation, less crystalline polymer tends to be more degradable [24]. While the PLLA-*r*-cyclic carbonates prepared by Sn1 did not show melting point, the RLT97-Sm1 possessed melting point, indicating that the former is amorphous and the latter is semicrystalline possibly due to partial block nature. Thus, the Sn initiator is superior to the Sm in the randomness in the random copolymerization. This could be the reason for lower compost degradability of the random copolymers produced by Sm1 than those produced by Sn1. Rather low molecular weight of the RLT91-Sn1 could also be a reason for its high compost degradability.

The D,L-LA-containing polymers showed higher compost degradability than those of the L-LA-containing polymers, however, the effect of the incorporated cyclic carbonates was more drastic for the copolymers based on L-LA than those based on D,L-LA. Homopoly(D,L-LA) can be completely degraded within 21 days (Fig. 3, **c**). Most of the PLLA-co-poly(cyclic carbonates)s showed comparable or lower degradabilities in comparison with PDLLA, except for the triblock copolymers produced by Sm2 (Fig. 3, **a** and Fig. 4, **a**). Although the reason is not clear why the triblock copolymerization by Sm2 is so particularly effective to improve compost degradability of PDLLA, we speculate that the initiating diphenylbutadiene moiety might somewhat affect the morphology of the resulting copolymer.

In the enzymatic degradation of L-LA-containing polymers, the copolymerization of L-LA with TMC was also quite effective to improve the degradability of PLLA. In particular, triblock copolymerization by Sm2 (Fig. 5, **a**) enhanced degradability of PLLA, presumably due to appropriate morphology and crystallinity arisen from the accompanying epimerization.

In sharp contrast, a triblock copolymer prepared by Sn2, TRT92-Sn2, exhibited high degradability. A random copolymer, RRT87-Sm1, was also highly degradable. Other copolymerizations of D,L-LA and TMC did not improve the degradability of homopoly(D,L-LA). On the other

hand, a diblock copolymer of D,L-LA and DTC by Sm1 and a random copolymer by Sn1 were rapidly degraded by Proteinase K. Thus, enzymatic degradability of D,L-LA-containing polymers can be improved by appropriate combination of polymerization method and initiator depending on the used cyclic carbonate as a comonomer.

5. Conclusions

The comparison of $(C_5Me_5)_2SmMe(THF)$ (Sm1) and $[(C_5Me_5)_2Sm]_2-(PhC=C=C=CPh)$ (Sm2), with tin compounds, $Bu_2Sn(OMe)_2$ (Sn1) and $Bu_2Sn(OCH_2CH_2CH_2O)$ (Sn2), for the preparation of random and diblock copolymers composed of L-LA or D,L-LA and TMC or DTC together with triblock copolymers was studied, and the biodegradabilities of the resulting copolymers with proteinase K and a compost were examined. In comparison of the catalytic behaviors between the samarium initiators and tin initiators, the samarium initiators are good at the control of the molecular weight distribution, while polymer yields in the tin systems were higher than those in the samarium systems. In the random copolymerization of lactide and cyclic carbonates under high LA/cyclic carbonate ratio, the tin initiator afforded amorphous polymers, while that produced by the samarium initiator was semicrystalline. The copolymerization of L-LA with cyclic carbonates by Sm1 or Sm2 afforded copolymers with relatively low melting points ($<160\text{ }^\circ\text{C}$) due to the accompanying epimerization. In the degradation of L-LA-containing polymers with a compost, random copolymers of L-LA with TMC or DTC prepared by Sn1 were most degradable because of their amorphousness. The triblock copolymerization of D,L-LA with cyclic carbonates by Sm2 was found to be effective to enhance compost degradability of D,L-LA-containing polymers. The complex Sm2 also produced PLLA-*b*-PTMC-*b*-PLLA, which possess good enzymatic degradability by Proteinase K. In a series of D,L-LA-containing copolymers, TRT92-Sn2 and DRD92-Sm2 were significantly more degradable than homopoly(D,L-LA). Thus, degradability of poly(lactide)s can be effectively improved by copolymerization with cyclic carbonates.

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