

Synthesis, Physical Properties, and Crystallization of Optically Active Poly(L-phenyllactic acid) and Poly(L-phenyllactic acid-co-L-lactic acid)

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ABSTRACT: Optically active poly(L-phenyllactic acid) (Ph-PLLA), poly(L-lactic acid) (PLLA), and poly(L-phenyllactic acid-co-L-lactic acid) with weight-average molecular weight exceeding $6 \times 10^3 \text{ g mol}^{-1}$ were successfully synthesized by acid catalyzed direct polycondensation of L-phenyllactic acid and/or L-lactic acid in the presence of 2.5–10 wt % of *p*-toluenesulfonic acid. Their physical properties and crystallization behavior were investigated by differential scanning calorimetry, thermogravimetry, and polarimetry. The absolute value of specific optical rotation ($[\alpha]_{589}^{25}$) for Ph-PLLA ($-38 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$) was much lower than that of $[\alpha]_{589}^{25}$ for PLLA ($-150 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$), suggesting that the helical nature was reduced by incorporation of bulky phenyl group. PLLA was crystallizable during solvent

evaporation, heating from room temperature, and cooling from the melt. Incorporation of a very low content of bulky phenyllactyl units even at 4 mol % suppressed the crystallization of L-lactyl unit sequences during heating and cooling, though the copolymers were crystallizable for L-phenyllactyl units up to 6 mol % during solvent evaporation. The activation energy of thermal degradation (ΔE_{td}) for Ph-PLLA (200 kJ mol^{-1}) was higher than that for PLLA (158 kJ mol^{-1}). The ΔE_{td} for the copolymers increased with an increase in L-phenyllactyl unit content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3954–3962, 2008

Key words: crystallization; polyesters; poly(L-lactide); poly(L-phenyllactide); thermal properties

INTRODUCTION

Poly(L-lactic acid) (PLLA), a biodegradable polyester produced from renewable resources such as starch, has been intensively studied and is now widely used in industrial and commodity applications as well as biomedical and pharmaceutical applications, due to the reduced cost by mass production.^{1–11} Recently, PLLA is used as the parts of automobiles and the housing of personal computers and mobile phones.

Copolymerization is one of most effective methods to improve or manipulate the physical properties and biodegradation of PLLA-based polymers. Among the

comonomers of L-lactide, glycolide, D-lactide, and ϵ -caprolactone were frequently utilized to vary physical properties and biodegradation rate. Surprisingly, with respect to the synthesis and characterization of poly(lactic acid) (PLA) with its hydrogen in methyl group substituted with other groups, only few examples have been published. Reported substituted PLA includes poly(phenyllactic acid) and poly(malic acid), wherein hydrogen in methyl group is substituted with phenyl and carboxyl groups, respectively.^{12,13} Furthermore, methyl-, trimethyl-, and pentyl-substituted PLAs, that is, poly(ethylglycolide), poly(isobutylglycolide), and poly(hexylglycolide) were synthesized by ring-opening polymerization of substituted lactides, and their thermal properties were investigated.¹⁴ These substituted PLAs have higher thermal stability when compared with that of nonsubstituted PLA. Also, although the copolymers composed of lactyl units and substituted lactyl units were synthesized,^{13,15–17} their physical properties and crystallization have not been reported.

The molecular structures including optical purity of these homo- and copolymers largely affect the physical properties, crystallization, and biodegradation behavior. The applications of the polymers will

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be determined by the physical and chemical properties, such as optical activity, glass transition and thermal degradation temperatures, and by the crystallization and biodegradation behavior. For example, the optical activity of polymer solution is closely related to that of its uniaxially oriented solid-state materials. Related to the high optical activity, uniaxially oriented PLLA can be utilized as light modulation materials.¹⁸ The glass transition temperature or the softness at a fixed temperature is an essential factor to determine the material applications. Also, the thermal processing temperatures should be selected carefully to avoid the thermal degradation of the polymers. Furthermore, the dimensional stability and biodegradation behavior of the polymers are controllable by altering crystallinity and, therefore, the information on crystallization behavior is fundamental for manipulating crystallinity. Because of aforementioned reasons, it is crucial to obtain the basic information on the physical properties and crystallization behavior. However, in previous reports the substituted lactic acid units were optically inactive or the physical properties and crystallization behavior of homo- and copolymers of substituted lactic acids were not studied in detail. If the optically inactive substituted and nonsubstituted PLAs were used, the disturbance effects of bulky group on the formation of helical structure (therefore, the effects on the optical, glass transition, and thermal degradation properties) and on the crystallization could not be estimated because optically inactive substituted and nonsubstituted PLAs would not form helical structure and noncrystallizable.

The purpose of the present study was to obtain the basic information of optically active phenyl-substituted PLA polymers, poly(L-phenyllactic acid) (Ph-PLLA), and poly(L-phenyllactic acid-co-L-lactic acid) on physical properties and crystallization behavior. For this purpose, optically active Ph-PLLA and poly(L-phenyllactic acid-co-L-lactic acid), together with PLLA, were synthesized by acid-catalyzed polycondensation from L-phenyl lactic acid and L-lactic acid. The physical properties and crystallization of thus prepared polymers were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), and polarimetry.

EXPERIMENTAL

Materials

Homopolymers, that is, Ph-PLLA and PLLA, and copolymers, that is, poly(L-phenyllactic acid-co-L-lactic acid), which molecular structures are shown in Figure 1, were synthesized by polycondensation of L-phenyllactic acid (i.e., S-phenyllactic acid, 98%,

Sigma-Aldrich) and/or L-lactic acid (85 wt %, Sigma-Aldrich, St. Louis, MO) using *p*-toluenesulfonic acid (monohydrate, 99%, guaranteed grade, Nacalai Tesque, Kyoto, Japan) as the catalyst. The polycondensation of L-phenyllactic acid and L-lactic acid was carried out without or with 2.5 and 10 wt % of *p*-toluenesulfonic acid under a constant nitrogen gas flow at 130°C under an atmospheric pressure for 5 h and then at a reduced pressure of 2.4 kPa (18 mmHg) for 24 h in the case of L-phenyllactic acid and for 6 h in the case of L-lactic acid. The reaction temperature of 130°C was selected to perform polycondensation in the molten state of L-phenyl lactic acid [melting temperature (T_m) of 122–124°C]. The synthesis of copolymers having different L-phenyllactyl unit contents were carried out with the same procedures of Ph-PLLA.

Thus synthesized polymers were purified by the extraction with methanol for at least 48 h and then dried in reduced pressure for at least 7 days. During purification, methanol was replaced twice with three and 24 h of extraction. The specimens for DSC and TG were prepared by casting the chloroform solution with a polymer concentration of 1.0 g dL⁻¹ onto a petri-dish, followed by solvent evaporation at 25°C for ~ 2 days. The obtained specimens were dried *in vacuo* for at least 1 week. The amorphous-made specimens were prepared as follows. Each of the specimens was sealed in a DSC aluminum cell and further sealed in a test tube under reduced pressure. The sealed specimens were melt in an oil bath kept at 200°C for 5 min, and then quenched at 0°C.

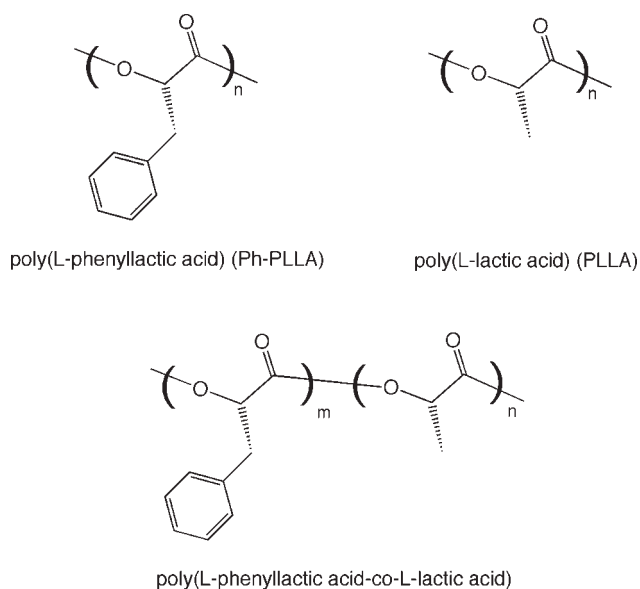


Figure 1 Molecular structures of Ph-PLLA, PLLA, and their copolymer.

TABLE I
The Molecular Characteristics and Thermal Degradation Properties of PLLA, Ph-PLLA, and Copolymers

Code	$M_w/10^3$ (g mol ⁻¹)	M_w/M_n	L-Phenylactyl unit content in the feed (mol %)	L-Phenylactyl unit content in the polymer ^a (mol %)	$[\alpha]_{589}^{25}$ (deg dm ⁻¹ g ⁻¹ cm ³)	T_{td}^0 (P) ^b (°C)	ΔE_{td}^b (kJ mol ⁻¹)
PLLA	9.8	2.4	0	0	-150	357.1	158.0
C4	8.4	3.2	5	4			
C6	10.5	2.6	10	6			
C31	10.9	4.2	25	31	-92	354.6	140.5
C54	7.2	2.0	50	54	-65	350.7	162.1
C79	13.0	2.0	75	79	-48	349.1	174.6
Ph-PLLA	6.7	2.9	100	100	-38	343.4	198.7

^a L-phenylactyl unit content was evaluated by ¹H NMR spectroscopy.

^b T_{td}^0 (P) is the peak temperature of derivative of weight remaining during thermal degradation at zero heating rate, whereas ΔE_{td} is the activation energy for thermal degradation.

Physical measurements and observation

The weight- and number-average molecular weights (M_w and M_n , respectively) of the purified polymers were evaluated in chloroform at 40°C using a Tosoh (Tokyo, Japan) GPC system with two TSK gel columns (GMH_{XL}) and polystyrene standards. Therefore, the M_w and M_n values are given relative to polystyrene. The specific optical rotation ($[\alpha]_{589}^{25}$) of polymers was measured in chloroform at a concentration of 1 g dL⁻¹ and 25°C using a JASCO DIP-140 polarimeter at a wave length of 589 nm. The L-phenylactyl unit contents of synthesized copolymers were determined from the 300 MHz ¹H NMR spectra obtained in deuterated chloroform (50 mg mL⁻¹) by a Varian Inova-400 Spectrometer using tetramethylsilane as an internal standard. The ratio of the integrated intensity at 1.6 ppm (methyl group of L-lactyl unit)^{19,20} to that at 3.0–3.2 ppm (methylene group of L-phenylactyl unit) was used to determine the chemical composition of the copolymers. The characteristics of the polymers are summarized in Table I. In the present study, poly(L-phenylactic acid-co-L-lactic acid) having an L-phenylactyl unit content of X mol % is abbreviated as CX.

The glass transition, cold crystallization, and melting temperatures (T_g , T_{cc} , and T_m , respectively) and enthalpies of cold crystallization and melting (ΔH_{cc} and ΔH_m , respectively) were determined with a Shimadzu (Kyoto, Japan) DSC-50 differential scanning calorimeter under a nitrogen gas flow at a rate of 50 mL min⁻¹. For investigating the crystallization during heating, the amorphous-made specimens were heated from room temperature to 200°C at a rate of 10°C min⁻¹ (Process I, crystallization was observed here). The crystallization during solvent evaporation was traced using as-cast specimens by the same procedure. For investigating the crystallization during cooling from the melt, as-cast specimens were heated from room temperature to 200°C at a rate of

10°C min⁻¹, kept at 200°C for 5 min, then cooled at -1°C min⁻¹ to about 50°C (Process II, crystallization was observed here). Wide-angle X-ray scattering (WAXS) measurements were carried out at 25°C using a RINT-2500 (Rigaku, Tokyo, Japan) equipped with a Cu-K α source ($\lambda = 0.1542$ nm).

RESULTS AND DISCUSSION

Synthesis

We selected 130°C the polycondensation temperature of L-phenylactic acid to carry out the reaction in the molten state of L-phenylactic acid ($T_m = 122$ –124°C) and to suppress thermal degradation (depolymerization and elimination, and so on) of the

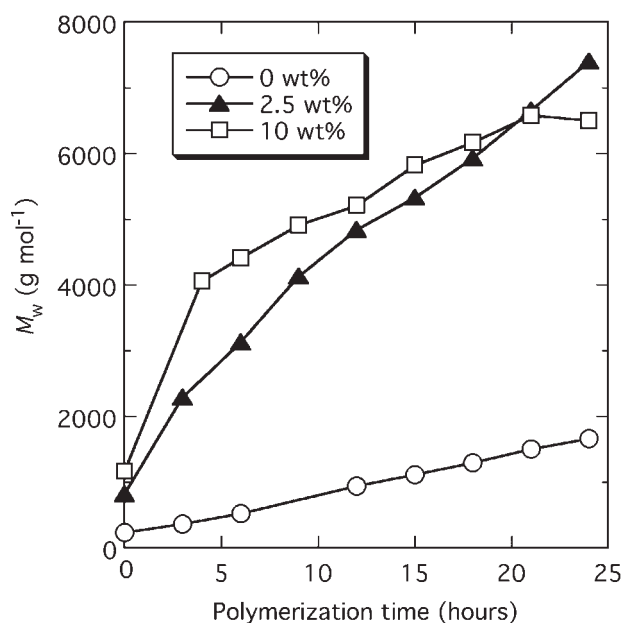


Figure 2 M_w change of Ph-PLLA synthesized at different concentrations of *p*-toluenesulfonic acid as a function of polymerization time.

synthesized polymers at high reaction temperature, although high temperature will increase reaction rate. Figure 2 shows the M_w change of Ph-PLLA synthesized from L-phenyllactic acid during polycondensation with different concentrations of *p*-toluenesulfonic acid. Here, the polymerization time means the reaction time under a reduced pressure (2.4 kPa) after 5 h of polymerization under an atmospheric pressure. In the first 5 h, the increase rate of M_w became higher with an increase in *p*-toluenesulfonic acid concentration, whereas in the polymerization time exceeding 5 h, the increase rate of M_w became maximum at 2.5 wt %. The M_w of Ph-PLLA synthesized with 2.5 and 10 wt % of *p*-toluenesulfonic acid increased over $6 \times 10^3 \text{ g mol}^{-1}$, whereas that synthesized without *p*-toluenesulfonic acid reached as low as about $2 \times 10^3 \text{ g mol}^{-1}$. The maximum value of M_w ($7.4 \times 10^3 \text{ g mol}^{-1}$) is comparable to those of copolymers synthesized by polycondensation ($1.0 \times 10^4 \text{ g mol}^{-1}$).¹⁶ These findings are indicative of the fact that *p*-toluenesulfonic acid has a significant catalytic effect on polycondensation of phenyllactic acid. From the final M_w at 24 h indicates that the most favorable concentration is 2.5 wt %. This concentration is in complete agreement with that used for synthesis of high molecular weight PLLA ($1.0 \times 10^5 \text{ g mol}^{-1}$) by polycondensation of L-lactic acid using diphenylether as the azeotropic solvent of water.²¹ For these reasons, we utilized the 2.5 wt % of *p*-toluenesulfonic acid for the synthesis of PLLA and copolymers. In addition to the increase in molecular weight, another evidence for polymerization of L-phenyllactic acid was the methine peak shift of ¹H NMR spectra from 4.5 ppm of the monomer to 5.3 ppm of the polymer. Such shift was reported for lactic acid polymerization from 4.0 ppm of the monomer to 5.2 ppm of the polymer.²²

The specific optical rotation ($[\alpha]_{589}^{25}$) values of Ph-PLLA and copolymers are shown in Table I. The absolute value of $[\alpha]_{589}^{25}$ for Ph-PLLA ($-38 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$) was much lower than that of $[\alpha]_{589}^{25}$ for PLLA ($-150 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$). The low absolute value of Ph-PLLA is partly due to the higher molecular weight of L-phenyllactyl unit (molecular weight = 148.2 g mol^{-1}) of Ph-PLLA when compared with that of L-lactyl unit (molecular weight = 72.1 g mol^{-1}) of PLLA. However, this cannot explain such a large decrease in $[\alpha]_{589}^{25}$. Another probable reason is the reduced helical nature of Ph-PLLA in solution when compared with that of PLLA because of incorporation of bulky phenyl group. The L-phenyllactyl unit contents in the polymers estimated by ¹H NMR spectroscopy are tabulated in Table I. As seen, the L-phenyllactyl unit content in the polymer is in good agreement with that in the feed, suggesting that the similar reactivities of L-phenyllactic acid and L-lactic acid during polycondensation and that the two

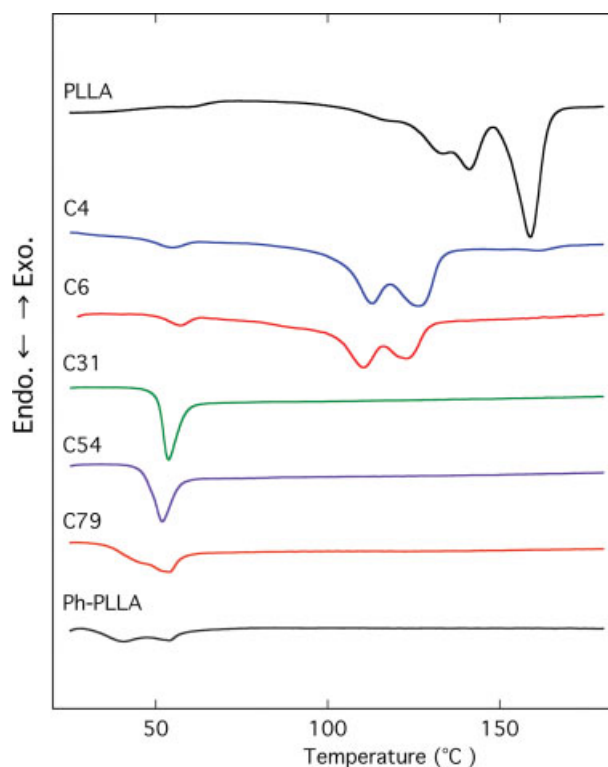


Figure 3 DSC thermograms of as-cast PLLA, Ph-PLLA, and their copolymers during heating from room temperature (Process I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

monomers were randomly distributed in the copolymers.

Crystallization during solvent evaporation

Figure 3 shows the DSC thermograms of as-cast PLLA, Ph-PLLA, and their copolymers during heating from room temperature and thermal properties obtained from this figure are summarized in Table II. As seen in Figure 3, PLLA, C4, and C6 had glass transition and melting peaks at 40–55 and 110–160°C, respectively, whereas C31, C54, C79, and Ph-PLLA had only glass transition peak at 30–50°C. The melting peak temperature observed for PLLA, C4, and C6 shifted to a lower temperature and the melting peak area decreased with an increase in L-phenyllactyl unit content. The relatively low T_m of PLLA (160°C) should be due to its low molecular weight ($9.8 \times 10^3 \text{ g mol}^{-1}$), as reported in a previous study.²³ The multiple peaks observed for PLLA, C4, and C6 are attributable to the melting and recrystallization of unstable crystallites during heating. The T_m values of C4 and C6 (123 and 127°C, respectively) are very close to that of L-phenyllactic acid (122–124°C). However, T_m value of C6 is higher than that of L-phenyllactic acid and multiple melting peaks as observed for C4 and C6 will not appear for

TABLE II
Glass Transition, Crystallization, and Melting Properties of PLLA, Ph-PLLA, and Copolymers During Heating (Process I) and Cooling from the Melt (Process II)

Code	Heating of as-cast specimens (Process I)			Cooling of melted as-cast specimens (Process II)		Heating of melt-quenched specimens (Process I)				
	T_g^a (°C)	T_m^a (°C)	ΔH_m^a (J g ⁻¹)	$T_{cc}(P)^b$ (°C)	ΔH_{cc}^b (J g ⁻¹)	T_g^a (°C)	$T_{cc}(P)^b$ (°C)	T_m^a (°C)	ΔH_{cc}^b (J g ⁻¹)	ΔH_m^a (J g ⁻¹)
PLLA	52.7	133.5, 141.3, 158.9	62.7	112.5	54.6	46.9	98.0	154.6	-48.5	48.0
C4	46.7	113.0, 126.5	34.6	-	0	45.5	-	-	0	0
C6	50.4	110.2, 122.8	25.7	-	0	51.2	-	-	0	0
C31	50.6	-	0	-	0	40.9, 44.6	-	-	0	0
C54	47.2	-	0	-	0	44.7	-	-	0	0
C79	36.3, 48.6	-	0	-	0	43.5	-	-	0	0
Ph-PLLA	31.5, 46.9	-	0	-	0	34.9	-	-	0	0

^a T_g , T_m , and ΔH_m are glass transition temperature, melting temperature, and melting enthalpy, respectively.

^b $T_{cc}(P)$ and ΔH_{cc} are peak temperature and enthalpy of cold crystallization, respectively.

low molecular weight compounds. With respect to crystallizability, it is reported that at least 7.2–15 L-lactyl unit sequences (molecular weight of about 520–1100 g mol⁻¹) are required to show the crystallizability.^{20,24–26} All the polymers used in the present study had sufficiently higher molecular weights than these critical values to show the crystallizability, if they have. Therefore, the fact that no melting peak was observed for C31, C54, C79, and Ph-PLLA reflects that these polymers with high L-phenyl lactyl units are noncrystallizable during solvent evaporation.

Crystallization during cooling and heating

Figure 4 shows the DSC thermograms of as-cast PLLA, Ph-PLLA, and their copolymers during cooling from the melt. Only PLLA had crystallization peak at around 100°C, whereas no crystallization peak was observed for the copolymers containing L-phenyllactyl units, reflecting that only PLLA is crystallizable, whereas the homopolymer and all the copolymers of L-phenyllactic acid are noncrystallizable during cooling from the melt. It is interesting to note that once C4 and C6 were melt, they showed no crystallizability during cooling. The thermal properties obtained from Figure 4 are tabulated in Table II. Figure 5 shows the DSC thermograms of amorphous-made Ph-PLLA, PLLA, and their copolymers during heating from room temperature. For PLLA, glass transition, cold crystallization, and melting peaks were observed at around 55, 100, and 155°C, respectively. The thermal properties obtained from this figure are shown in Table II. Relatively low T_g , T_{cc} , and T_m values of PLLA in the present study are attributed to its low molecular weight.^{27,28} Only glass transition peak was seen for all homopolymer and copolymers of L-phenyllactic acid, reflecting the noncrystallizability of homopolymer and

copolymers of L-phenyllactic acid during heating from room temperature, similar to the case of cooling of as-cast specimens. The similar trend was observed for stereocopolymers of L-lactide and D-lactide.^{24,29} The comparison of DSC data for C4 and C6 in Figures 3–5 indicates that the presence of solvent enhanced the crystallization during solvent evaporation. It is probable that the presence of solvent molecules elevated the molecular mobility of C4 and C6,

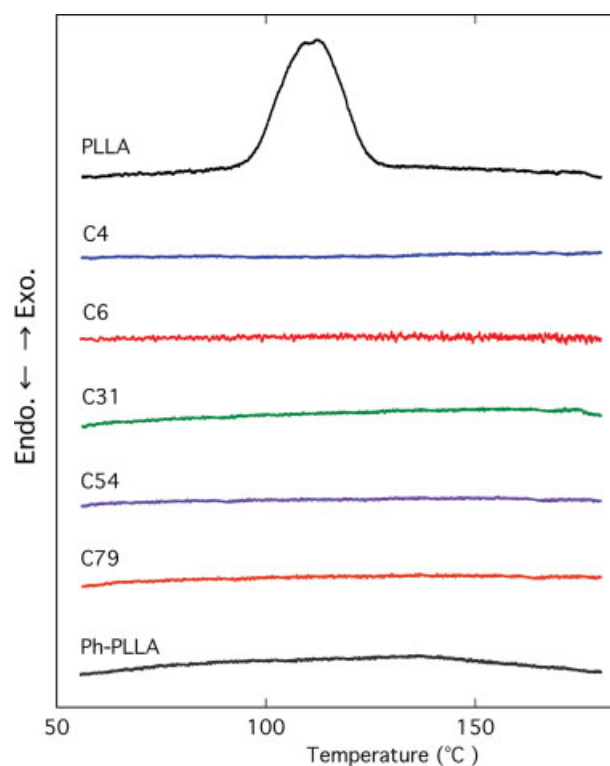


Figure 4 DSC thermograms of as-cast PLLA, Ph-PLLA, and their copolymers during cooling from the melt (Process II). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

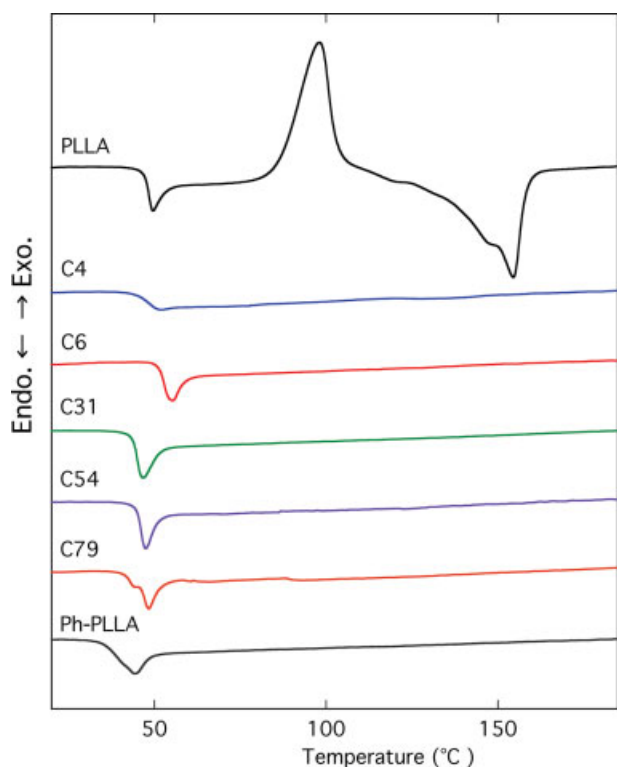


Figure 5 DSC thermograms of melt-quenched PLLA, Ph-PLLA, and their copolymers during heating from room temperature (Process I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

resulting in their crystallization during solvent evaporation.

The ΔH_m values of as-cast and melt-quenched specimens during heating from room temperature and the ΔH_{cc} values of as-cast specimens during cooling from the melt are summarized in Table II. Again, it is surprising that once the specimens were melt, the crystallizability of L-lactyl unit sequences during heating and cooling was lost even with the incorporation of 4 mol % (8 wt %) of L-phenyllactyl units. For as-cast specimens during cooling and melt-quenched specimens during heating, the critical content of comonomer above which L-lactyl unit sequences loses the crystallizability was 0–4 mol % (0–8 wt %) for L-phenyllactyl unit, which is comparable to 5–8 mol % (5–8 wt %) for D-lactyl unit.²⁴ This indicates that D-lactyl unit having the same size of L-lactyl unit, but the reverse configuration from that of L-lactyl unit has a disturbance effect on the crystallization of L-lactyl unit sequences, comparable to that of L-phenyllactyl unit having bulky phenyl group and the same configuration with that of L-lactyl unit.

Thermal degradation

The starting, peak, and ending temperatures of thermal degradation [$T_{td}(S)$, $T_{td}(P)$, and $T_{td}(E)$, respec-

tively] were estimated from thermal weight loss curves by the procedures shown in Figure 6. That is, $T_{td}(S)$ and $T_{td}(E)$ are the intersection temperatures of the base lines for lower and higher temperature ranges and the tangent line for the thermal weight loss curve. For estimation of $T_{td}(P)$ from the differential curve of thermal weight loss, the intersection temperature of contact lines for lower and higher temperature ranges of the peak temperature was used instead of actual peak value, because the noisy differential curves can cause the large deviation from the real peak value. Moreover, obtained $T_{td}(S)$, $T_{td}(P)$, and $T_{td}(E)$ were plotted against heating rate (ϕ) and the extrapolation of $T_{td}(S)$, $T_{td}(P)$, and $T_{td}(E)$ data lines to $\phi = 0$ gave the $T_{td}^0(S)$, $T_{td}^0(P)$, and $T_{td}^0(E)$ when ϕ approaches zero [$T_{td}^0(S)$, $T_{td}^0(P)$, and $T_{td}^0(E)$, respectively]. Figure 7 shows the $T_{td}^0(S)$, $T_{td}^0(P)$, and $T_{td}^0(E)$ of Ph-PLLA, PLLA, and copolymers. As seen from Figure 7, $T_{td}^0(P)$ and $T_{td}^0(E)$ decreased monotonously with increasing L-phenyllactyl unit content or decreasing degree of polymerization. Also, $T_{td}^0(S)$ had the inclination to decrease with an increase in L-phenyllactyl unit content or with a decrease in degree of polymerization,

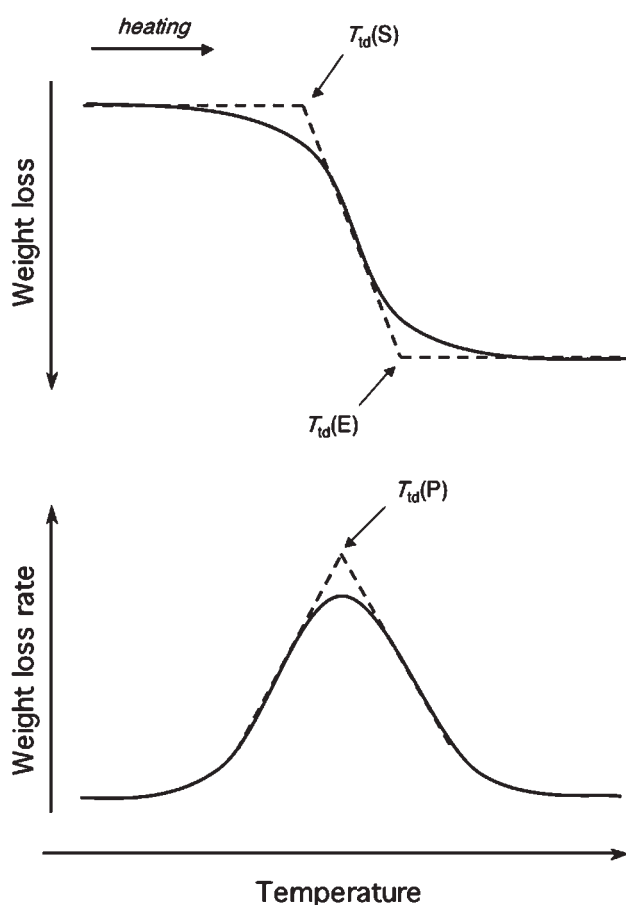


Figure 6 The procedures for estimating starting temperature [$T_{td}(S)$], peak temperature [$T_{td}(P)$], and ending temperature [$T_{td}(E)$] of thermal degradation.

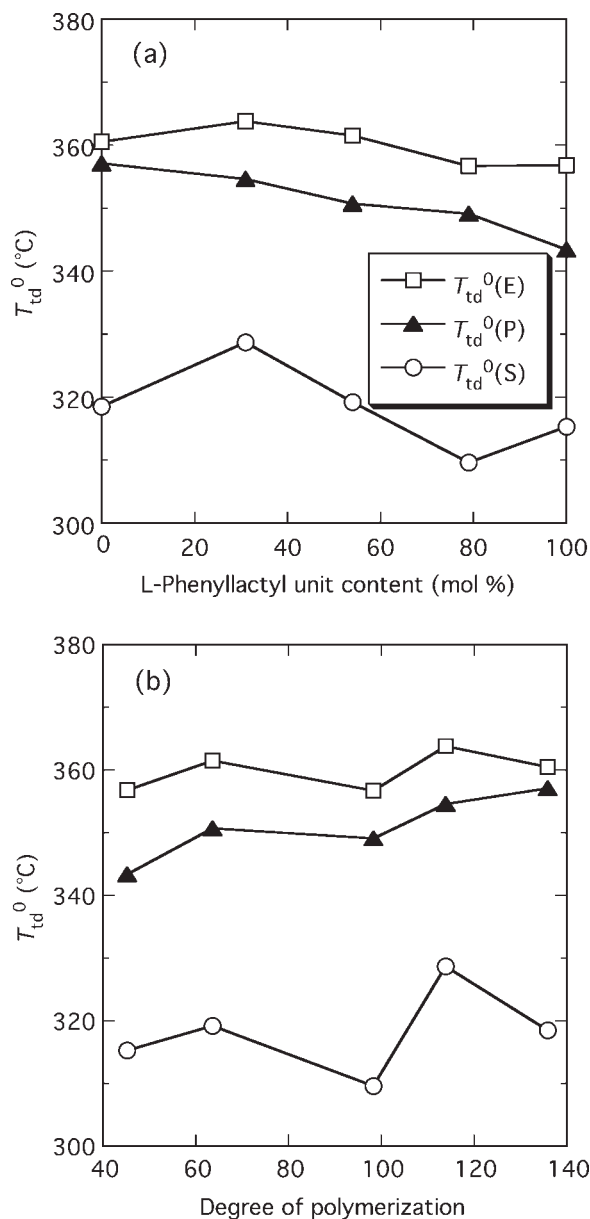


Figure 7 Starting, peak, and ending temperatures of thermal degradation at zero heating rate [$T_{td}^0(S)$, $T_{td}^0(P)$, and $T_{td}^0(E)$] of PLLA, Ph-PLLA, and copolymers as functions of L-phenyllactyl unit content (a) and degree of polymerization (b).

although $T_{td}^0(S)$ gave maximum and minimum at L-phenyllactyl unit content of 31 and 79 mol %, respectively, or at degree of polymerization of 114 and 98, respectively.

With an increase in degree of polymerization, thermal degradation temperatures are expected to shift to higher temperatures. The result in Figure 7(b) was consistent with this expectation. Therefore, the effects of two factors, L-phenyl lactyl unit content and degree of polymerization on thermal degradation temperatures, cannot be separately discussed. However, it is evident that the effect of L-phenyllac-

tyl unit content on thermal degradation temperatures was too small to overcome the effect of degree of polymerization. Such a small effect of L-phenyllactyl unit content can be explained as follows. The effect of reduced helical nature by incorporated bulky phenyl group, which will decrease intramolecular and intermolecular interaction and reduce the thermal degradation temperatures, should be balanced with the effect of bulkiness of the incorporated phenyl group, which will reduce chain mobility and increase the thermal degradation temperatures. The result in the present study is in contrast with the results reported for poly(ethylglycolide), poly(isobutylglycolide), and poly(hexylglycolide),¹⁴ wherein substituted PLA has higher thermal degradation temperatures when compared with that of PLLA. In the reported case, the polymers used were composed of equimolar D- and L-monomer units and optically inactive and, therefore, the effect of bulkiness of substituted group, not the effect of helical nature should have been dominant for determining thermal degradation temperature.

The activation energy for thermal degradation (ΔE_{td}) of PLLA, Ph-PLLA, and their copolymers was obtained using Kissinger eq. (1)^{30,31}:

$$d[\ln \phi / T_{td}(P)^2] / d[1/T_{td}(P)] = -\Delta E_{td} / R. \quad (1)$$

That is, $\ln \phi / T_{td}(P)^2$ against $1/T_{td}(P)$ according to eq. (1) and ΔE_{td} values of the polymers were estimated from the slope values of these plots. The obtained ΔE_{td} values are shown in Table I and plotted in Figure 8 as functions of L-phenyllactyl unit content and degree of polymerization. The obtained ΔE_{td} values of PLLA and Ph-PLLA were 158 and 199 kJ mol^{-1} , respectively. The ΔE_{td} value of PLLA is comparable to the ΔE_{td} values reported for PLLA, 72–103 kJ mol^{-1} (Babanalbandi et al.),³² 110 kJ mol^{-1} (Kopinke et al.),³³ and 80–160 kJ mol^{-1} (Aoyagi et al.),³⁴ 77–132 kJ mol^{-1} (Tsuji and Fukui),³⁵ 120–180 kJ mol^{-1} (Fan et al.),³⁶ and poly(DL-lactide) (PDLLA), 119 kJ mol^{-1} (McNeill and Leiper).³⁷ The wide variation of the reported values is attributable, the difference in the type and concentration of catalyst, the concentration of lactide,³⁸ and the polymer molecular weight, its distribution, and terminal group,³⁹ the method, procedure, and conditions for estimating ΔE_{td} .

The ΔE_{td} increased gradually with an increase in L-phenyllactyl unit content, although ΔE_{td} decreased slightly at L-phenyllactyl unit content of 31 mol %. In contrast, the ΔE_{td} decreased roughly with an increase in degree of polymerization, in contrast to the normally anticipated result. These findings here mean that L-phenyllactyl unit content is a dominant factor to determine ΔE_{td} . The effect of bulkiness of benzyl group in L-phenyllactyl unit when compared

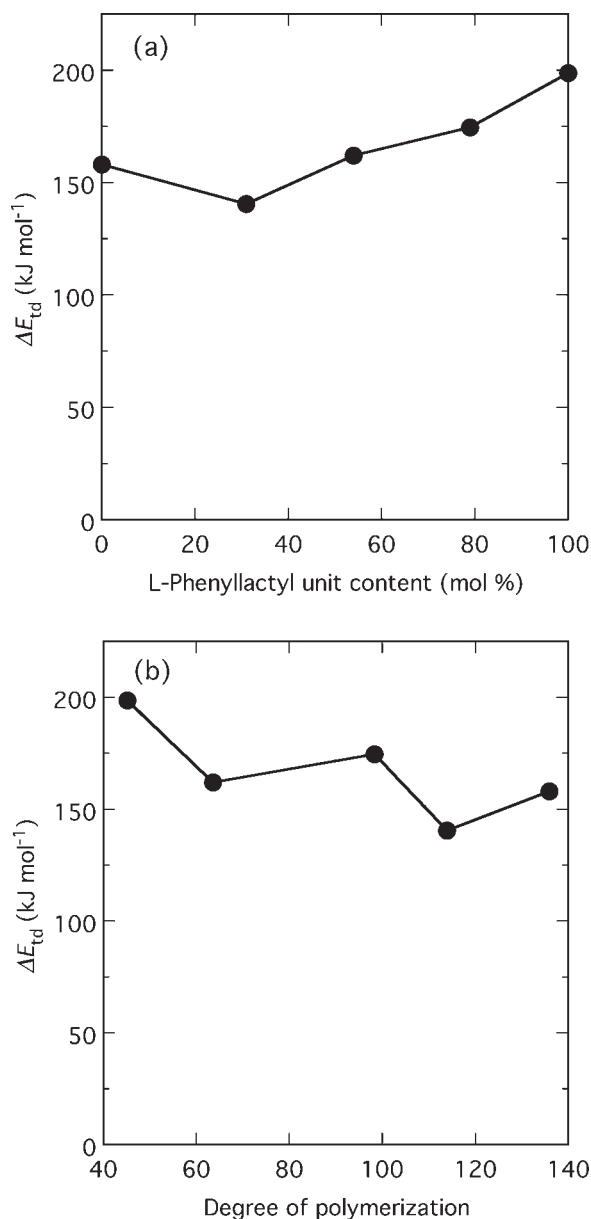


Figure 8 The activation energy for thermal degradation (ΔE_{td}) as functions of L-phenyllactyl unit content (a) and degree of polymerization (b).

with that of methyl group in L-lactyl unit, which is expected to increase ΔE_{td} , should be higher than the effect of reduced helical nature in incorporation of bulky benzyl group in L-phenyllactyl unit, which is anticipated to reduce ΔE_{td} .

CONCLUSIONS

From the aforementioned results, following conclusions can be derived for synthesis and properties of Ph-PLLA and poly(L-phenyllactic acid-co-L-lactic acid).

1. Ph-PLLA and poly(L-phenyllactic acid-co-L-lactic acid) with M_w exceeding $6 \times 10^3 \text{ g mol}^{-1}$ can

be successfully prepared with polycondensation of L-phenyllactic acid and L-lactic acid in the presence of 2.5–10 wt % of *p*-toluenesulfonic acid as the catalyst.

2. The absolute value of $[\alpha]_{589}^{25}$ for Ph-PLLA ($-38 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$) was much lower than that of $[\alpha]_{589}^{25}$ for PLLA ($-150 \text{ deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$). This result suggests that helical nature was reduced by the incorporation of bulky phenyl groups.
3. Ph-PLLA is noncrystallizable during solvent evaporation, cooling from the melt, and heating from room temperature. Incorporation of a very low concentration of L-phenyllactyl unit even at 4 mol % suppressed the crystallization of L-lactic acid copolymer during heating and cooling, although the copolymers were crystallizable for L-phenyllactyl units at least up to 6 mol % during solvent evaporation. This is indicative of the fact that the presence of solvent enhanced the crystallization of phenyl-substituted copolymers.
4. The ΔE_{td} for Ph-PLLA (200 kJ mol^{-1}) was higher than that for PLLA (158 kJ mol^{-1}). The ΔE_{td} for the copolymers increased with an increase in L-phenyllactyl unit content but decreased with an increase in degree of polymerization. This result is indicative of the fact that bulkiness of phenyl group is dominant for determining ΔE_{td} . However, the thermal degradation temperatures of the copolymers increased with a decrease in L-phenyllactyl unit content and with an increase in degree of polymerization, suggesting that the dominant factor is degree of polymerization.

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