Synthesis and Properties of Crystalline Dicarboxylated Poly(L-lactic acid) Prepolymers

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ABSTRACT: Crystalline dicarboxylated poly(L-lactic acid)s (dcPLLAs) with number-average molecular weights (M_n's) of 10^3 to 10^4 g/mol were synthesized via the melt polycondensation of L-lactic acid (LLA) in the presence of succinic anhydride (SAD), with tin(II) chloride and toluene-4-sulfonic acid as binary catalysts. They were characterized by end-group titration, ^{1}H-NMR, differential scanning calorimetry, and wide-angle X-ray diffraction. The terminal COOH percentage reached over 98%, and the molecular weight could be controlled by the molar ratio of LLA to SAD. The thermal behaviors depended on the molecular weight. The poly(L-lactic acid)s (PLLAs) crystallized slowly for $M_n \leq 2000$ but quickly for $M_n \geq 4000$. The crystallinity increased from 27 to 40% when M_n grew from 4000 to 10,000. With comparison to ordinary PLLA, the dcPLLA had the same crystallization structure but a slightly lower crystallizability. The glass-transition temperature was clearly higher than that of amorphous dcPLLAs. With a controllable molecular weight, high COOH percentage, and crystallinity, the dcPLLA with $M_n \geq 4000$ appeared to be a suitable prepolymer for the preparation of high-molecular-weight crystalline PLLA via chain extension. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3246–3251, 2011

Key words: biodegradable; crystallization; polycondensation

INTRODUCTION

Poly(L-lactic acid) (PLLA) is an important biobased and biodegradable polymer with tremendous market potential in packing materials, fibers, commodity plastics, biomaterials, and so on.[1,2] PLLA has been commercially produced with ring-opening polymerization technology at NatureWorks in the United States and Haizheng in China. However, the development of more cost-effective manufacturing technologies for high-molecular-weight and high-performance PLLA is still desired for large-scale applications.

The chain extension of low-molecular-weight PLLA prepolymer appears to be such a promising approach to synthesizing high-molecular-weight PLLA because of its low cost, which results from the direct use of L-lactic acid (LLA) instead of lactide and the rapid growth of the molecular weight within a short period of time. The chain extension of dihydroxylated PLLA with isocyanate is an effective way to synthesize high-molecular-weight PLLA and has been researched extensively.[3–7] However, the high reactivity, volatility, and toxicity of isocyanate impedes its practical application in the chain extension of PLLA. The chain extensions of dicarboxylated poly(L-lactic acid) (dcPLLA) with bisoxazoline[8] and diepoxide[9] seem to be better choices, especially for the latter. Diepoxide extender has a proper cost, appropriate reactivity, and good safety during utilization. In addition, new microstructures, such as side hydroxyl groups and long branched chains, can be introduced during chain extension.

In addition to the properties of the extender, the properties of the prepolymer are also very important for a successful chain-extension reaction. The requirements for dcPLLA include: (1) a high terminal COOH percentage to reach a high molecular weight, (2) a controllable molecular weight to control the final chain structure, and (3) a high crystallinity to provide an end product with proper crystallinity and thermal/mechanical properties. Hiltunen et al.[10] reported the synthesis of dihydroxylated and dcPLLA prepolymers via the stannous octoate catalyzed melt polycondensation of LLA, but the prepolymers were all amorphous. As one of a series of studies on the synthesis of crystalline PLLA via chain extension, we report in this article on the synthesis and properties of crystalline dcPLLA prepolymers with high terminal COOH percentages, controlled molecular weights, and good crystallinity through the melt polycondensation of LLA catalyzed

by tin(II) chloride dihydrate ($SnCl_2$) and toluene-4-sulfonic acid (TSA).

EXPERIMENTAL

Materials

Aqueous LLA (90 wt % content, 98% optical purity according to the provider, Jiangxi Musashino Bio-Chem Co., Nanchang, China), succinic anhydride (SAD; Shanghai Lingfeng Chemical Reagent Co., Shanghai, China), TSA (Sinopharm Chemical Reagent Co., Shanghai, China), and $SnCl_2 \cdot 2H_2O$ (Shanghai No. 4 Reagent and H. V. Chemical Co., Shanghai, China) were used as received.

Synthesis of the dcPLLAs

Aqueous LLA (180 g) was added to a 250-mL, four-necked flask equipped with a mechanical stirrer and connected to a vacuum system. It was dehydrated in the presence of $TSA \cdot H_2O$ under about 3000 Pa at 130°C for 2 h. Then, a small amount of SAD was added, and the mixture was oligomerized under 300–500 Pa at 150°C for 2 h. Finally, $SnCl_2 \cdot 2H_2O$ was added, and the oligomers were melt-polycondensed under 200–300 Pa at 180°C for 7–12 h, depending on the LLA/SAD molar ratio. For comparison, two ordinary PLLA samples were synthesized in the absence of SAD. The amount of $SnCl_2 \cdot 2H_2O$ was 0.3 wt % on the basis of the mass of LLA. TSA was used at a 1 : 1 TSA/$SnCl_2$ molar ratio. The amount of SAD is detailed in Table I and depended on the designed molecular weights of the prepolymers.

Characterization

^{1}H-NMR spectra were recorded with a Bruker ADVANCE2B 400-MHz spectrometer (Rulle, Germany) in $CDCl_3$ containing 0.03 vol % tetramethylsilane, with styrene as an internal standard. The sample concentration was around 5 wt %.

The acid values of the products ($v_{COOH,titr}$) were determined by the titration of a chloroform solution of the sample with a 0.1 mol/L KOH/ethanol solution at room temperature, with bromthymol blue as an indicator. As the ^{1}H-NMR spectra indicated that trace SAD remained in the product, the true acid value (v_{COOH}) of dcPLLA was calibrated with eq. (1), in which the contribution of unreacted SAD ($v_{COOH,SAD}$) was subtracted. However, the hydroxyl value (v_{OH}) was so small that it was difficult to precise measure it by titration. So ^{1}H-NMR analysis was used instead to determine it, with styrene as an internal reference.[11] It was calculated with eq. (2), where $A_{t\text{-}CH}$ is the integral area of the chemical shift at 4.33 ppm of methine, which directly connected with the OH end groups in PLLA; $A_{St\text{-}CH}$ is the integral area of the chemical shift of α-H at 6.78–6.71 ppm in styrene; n_{St} is the molar number of styrene added; m_s is the weight of the sample; and 56.1 is the molecular weight of KOH. The assignment of the chemical shifts is shown in the Results and Discussion section:

$$v_{COOH} = v_{COOH,titr} - v_{COOH,SAD} \qquad (1)$$

$$v_{OH} = \frac{(A_{t\text{-}CH}/A_{St\text{-}CH})n_{St}}{m_s} \times 56.1 \times 10^3 \qquad (2)$$

The number-average molecular weight (M_n) was calculated from the previously discussed end-group analysis with eq. (3), on the basis of the fact that there were two end groups (COOH and OH) per chain. We also directly calculated it from the ^{1}H-NMR spectra with eq. (4), supposing there was one succinate moiety per chain. In the equation, A_{CH} is the integral areas of the chemical shift of all methines, A_{CH2} is the integral area of the chemical shift of CH_2 in the succinate moiety, and $M_{lactate}$ and M_{SAD} are the molecular weights of the lactate unit (72 g/mol) and SAD (100 g/mol), respectively:

$$M_{n,EG} = \frac{56.1 \times 2 \times 10^3}{(V_{COOH} + V_{OH})} \qquad (3)$$

TABLE I
Reaction Conditions and Molecular Characteristics of the Ordinary PLLAs and dcPLLAs

Run	Calculated M_n (g/mol)	N_{LLA}/N_{SAD}	Time (h)	Yield (%)	Lactide (wt %)[a]	SAD (wt %)[b]	v_{COOH} (mg/g)	v_{OH} (m/g)	COOH (%)	$M_{n,EG}$ (g/mol)	$M_{n,NMR}$ (g/mol)
PLLA1	–	–	6	85.0	2.5	–	25.1	25.1	50.0	2,200	2,600
PLLA2	–	–	8	84.8	2.7	–	6.3	6.3	50.0	8,900	14,000
dcPLLA1	1,000	14	7	83.7	2.8	0.25	85.8	1.0	98.8	1,200	1,300
dcPLLA2	2,000	28	9	83.5	2.4	0.23	44.9	0.9	98.0	2,300	2,800
dcPLLA3	4,000	56	10	83.5	2.7	0.07	24.8	0.3	98.8	4,200	5,200
dcPLLA4	6,000	80	11	83.0	3.2	0.03	19.9	0.5	97.5	5,200	6,900
dcPLLA5	10,000	140	12	82.3	3.5	0.01	12.1	0.1	99.2	9,300	14,100

[a] Weight percentage of the byproduct lactide and residual SAD in the ordinary PLLAs or dcPLLAs.
[b] Weight percentage of residual SAD in the ordinary PLLAs or dcPLLAs.

$$M_{n,\text{NMR}} = \frac{A_{\text{CH}}}{A_{\text{CH2}}/4} \times M_{\text{lactate}} + M_{\text{SAD}} \qquad (4)$$

Differential scanning calorimetry (DSC) measurements were performed on a TA Q200 differential scanning calorimeter (American TA Corporation, USA, New Castle). The sample (–10 mg) was first heated from -30 to $180°C$ at a heating rate of $10°C/$min, maintained at $180°C$ for 3 min, then cooled down to $-30°C$ at $10°C/\text{min}$, maintained at $-30°C$ for 2 min, and finally heated to $180°C$ at $10°C/\text{min}$ again. We calculated the crystallinity from the melt enthalpy by rating it to the reference 100% crystalline PLLA (93.6 J/g).[12]

Wide-angle X-ray diffraction (WAXD) measurements were carried out on an X'Pert PRO diffractometer (Philips, Nethelands, Almelo) with Cu Kα radiation (wavelength = 1.5418 Å) for powdery PLLA samples (dcPLLA4 and PLLA2) that had been crystallized at $130°C$ for 1 h.

RESULTS AND DISCUSSION

Crystalline dcPLLAs were synthesized through melt polycondensation of LLA in the presence of a small amount of SAD, with $SnCl_2$/TSA as a binary catalyst. The synthetic route is depictured in Scheme 1. SAD was added after most of the water in aqueous LLA was removed to prevent hydrolysis. The reaction between SAD and the hydroxyl groups in LLA and its oligomer first formed dicarboxylated dcPLLA-I containing one lactic and one succinic carboxyl group. The succinic carboxyl of dcPLLA-I further reacted with the hydroxyl in the LLA oligomer to form dcPLLA-II containing two lactic carboxyl groups. During the reaction, TSA was added at the dehydration stage, and $SnCl_2$ was added at the melt polycondensation stage. Such a
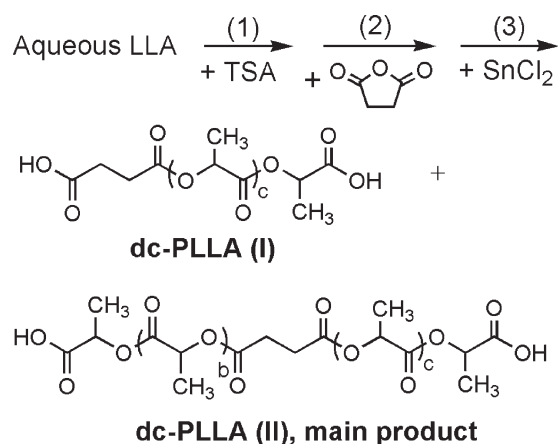
Scheme 1 Synthesis of dcPLLA via the melt polycondensation of LLA in the presence of SAD: (1) dehydration, (2) oligomerization, and (3) melt polycondensation.

catalyst addition policy was favorable for enhancing the rate of dehydration and oligomerization, as previously reported.[13] Namely, the synthesis procedure in this study was the same as that reported in ref. 13, except for the addition of SAD.

Five dcPLLA samples (dcPLLA1–dcPLLA5) with various molecular weights were prepared at a yield of about 83%. The reaction conditions and molecular characteristics are listed in Table I, together with those of ordinary PLLA samples containing one end OH group and one end COOH group. Their ^{1}H-NMR spectra and chemical shift assignments are illustrated in Figure 1.

In ordinary PLLA, the chemical shifts of methine and methyl in the middle of PLLA chain are at 5.19 ppm (1 in Fig. 1) and 1.59 ppm (2 in Fig. 1), and those of methine and methyl adjacent to the OH end group are at 4.4–4.35 ppm (1′ in Fig. 1) and 1.53–1.51 ppm (2′ in Fig. 1), respectively. The chemical shifts at 4.98–4.93 ppm (1‴ in Fig. 1) and 1.67–1.65 ppm (2‴ in Fig. 1) are attributed to methine and methyl in the byproduct lactide. Its amount was 3 ± 0.5 wt % (see Table I). The chemical shifts at 5.28–5.25 ppm (4 in Fig. 1), 5.79–5.75 ppm (5 in Fig. 1), 6.78–6.71 ppm (6 in Fig. 1), 7.44–7.42 ppm (7 in Fig. 1), 7.36–7.32 ppm (8 in Fig. 1), and 7.29–7.25 ppm (9 in Fig. 1) are assigned to styrene, the internal standard. In the dcPLLAs, the chemical shifts, shown at 1′ and 2′ in Figure 1, significantly decreased or disappeared, new chemical shifts at 2.83–2.68 ppm of CH_2 in succinic diester (3 in Fig. 1) and in carboxyl groups (3′ and 3″ in Fig. 1) appeared, and other chemical shifts remained almost unchanged. These results indicate the formation of succinic carboxyl groups via the reaction of SAD with OH and of succinic diesters via the further reaction of succinic carboxyl groups with OH. Chemical shift 3, shown in Figure 1, was much larger than those shown at 3′ and 3″ in Figure 1; this indicated that dcPLLA (II), with two lactic carboxyl end groups, was the dominant product. The chemical shift at 2.95 (3‴ in Fig. 1) was assigned to CH_2 of the unreacted SAD. Its amount, calculated from ^{1}H-NMR spectra, ranged from 0.25 to 0.01 wt % and decreased with decreasing SAD feed ratio, as shown in Table I.

End-group analysis indicated that the content of COOH end group in the dcPLLAs was over 98%. Such a high COOH content was beneficial to the synthesis of high-molecular-weight PLLA through the chain extension of dcPLLA.

The role SAD played in the polycondensation of LLA was not only the conversion of OH to COOH end groups but also the control of the number-average polymerization degree (X_n) of dcPLLA. As shown in eqs. (5) and (6), X_n was determined by the molar ratio (r) of the OH group in LLA to the whole COOH group in LLA and SAD (two COOH
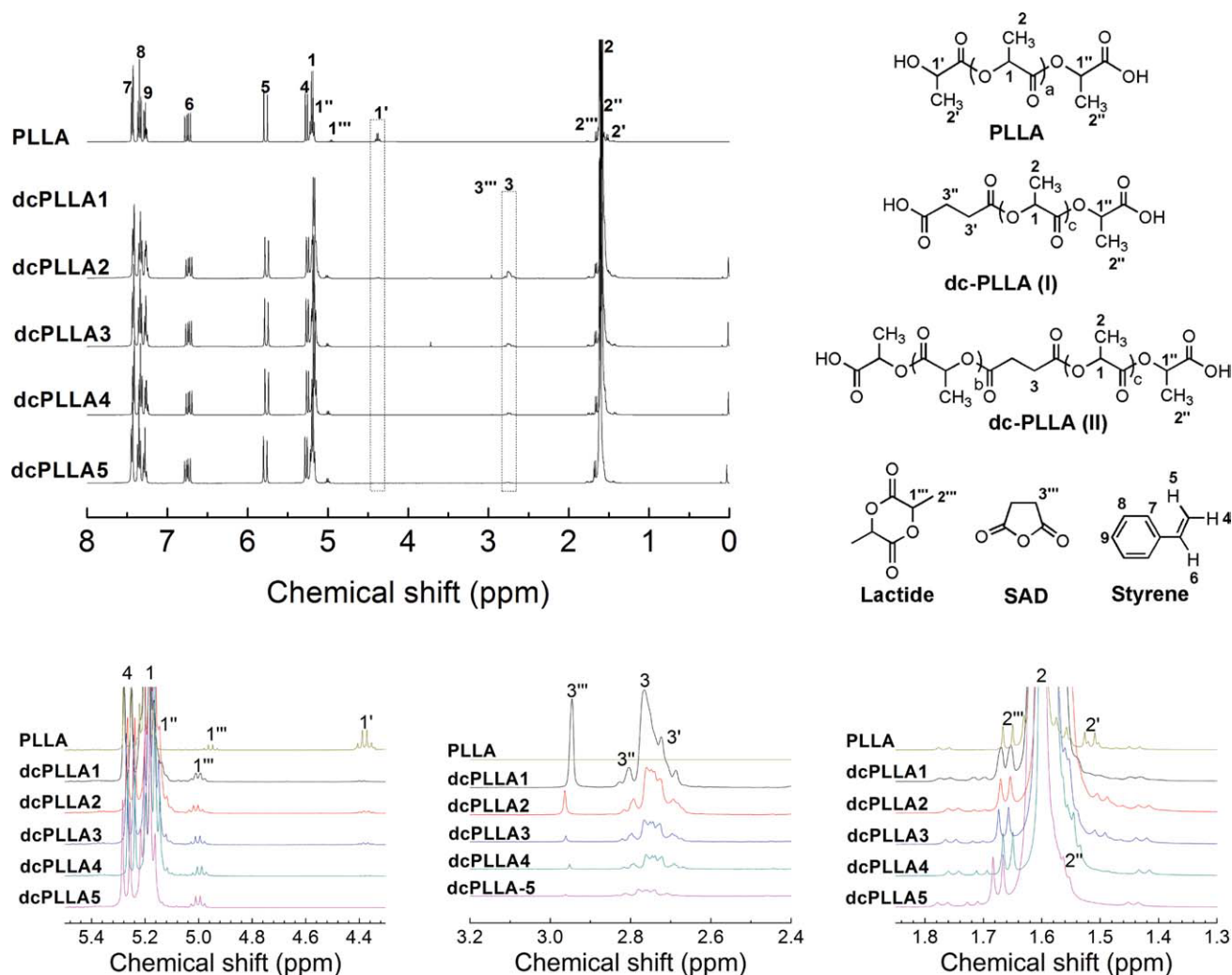
Figure 1 ^{1}H-NMR spectra and chemical shift assignments of ordinary PLLA and dcPLLA1–dcPLLA5. Styrene was used as an internal standard. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

groups were accounted for in one SAD molecule) or the molar ratio of LLA to SAD (N_{LLA}/N_{SAD}). Five dcPLLA samples, with designed M_n's ranging in 10^3 to 10^4 g/mol, were synthesized by an increase in the N_{LLA}/N_{SAD} ratio from 14 to 140. The number-average molecular weights measured from end-group analysis ($M_{n,EG}$) and directly from ^{1}H-NMR ($M_{n,NMR}$) listed in Table I both agreed well with the theoretical ones. Therefore, dcPLLAs with various molecular weights could be facilely synthesized by the simple tuning of the N_{LLA}/N_{SAD} ratio:

$$X_n = \frac{1+r}{1-r} = \frac{N_{LLA}}{N_{SAD}} + 1 \qquad (5)$$

$$r = \frac{N_{OH}}{N_{COOH}} = \frac{N_{LLA}}{N_{LLA} + 2N_{SAD}} = \frac{N_{LLA}/N_{SAD}}{N_{LLA}/N_{SAD} + 2} \qquad (6)$$

In addition to a high COOH content and controlled molecular weight, high crystallinity is

another important requirement for dcPLLA in the synthesis of PLLA materials with proper crystallinity. It was reported that the stannous octoate catalyzed melt polycondensation of LLA in the presence of adipic acid produced amorphous dcPLLAs because of the racemization of PLLA.[10] $SnCl_2$/TSA is a better binary catalyst for depressing racemization during the melt polycondensation of PLLA and, therefore, can be used to produce crystalline PLLA.[14] In our previous study,[13] we found that a new catalyst addition policy, that is, adding TSA at the dehydration stage and then $SnCl_2$ at the melt polycondensation stage, not only accelerated the reaction but was also beneficial in further depressing racemization. Using $SnCl_2$/TSA with such an addition policy, we produced crystalline dcPLLAs in this study, as indicated by the DSC curves shown in Figure 2.

In the first heating scan, all five samples experienced glass transition and melting, but only samples
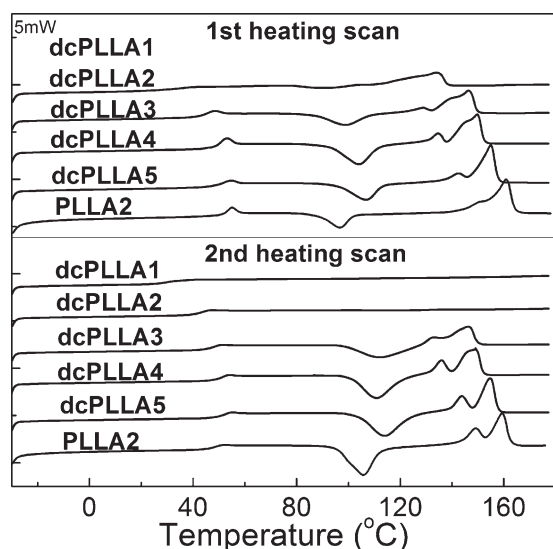
Figure 2 DSC curves of dcPLLAs with various molecular weights (dcPLLA1–dcPLLA5) and PLLA2.

with $M_n \geq 2000$ experienced cool crystallization at heating rate of 10°C/min. In the cooling scan (−10°C/min, curves not shown), glass transition occurred, but melt crystallization did not take place for all of the samples. In the second heating scan at 10°C/min, all five samples experienced glass transition, but only samples with $M_n \geq 4000$ clearly experienced cool crystallization and melting. The detailed thermal transition characteristics [glass-transition temperature (T_g), cold crystallization temperature T_c, melting temperature (T_m), and crystallinity] are listed in Table II. The results suggest that slow cooling after melt polycondensation led to a higher crystallinity than a standard cold crystallization at a heating rate of 10°C/min, especially for the samples with a lower molecular weight.

The behavior of thermal transition depended on not only the heat history but also on the molecular weight. The crystallization ability of dcPLLA increased with its M_n in the experimental molecular weight range. dcPLLAs with $M_n \leq 2000$ crystallized, but the crystallization rate was slow, and the crystallinity was low. However, dcPLLAs with $M_n \geq 4000$ crystallized fac-

ilely and reached crystallinity ranging from 27 to 40% under nonisothermal cold crystallization at 10°C/min. Such a molecular weight dependence was mainly attributed to a low nucleation ability in the low-molecular-weight range. A similar molecular weight dependence on the crystallization of ordinary PLLA was reported in our previous article.[15]

The cold-crystallized PLLA melted in the melt-recrystallization mechanism,[16] exhibiting double melting peaks. The low melt peak was attributed to the melting of the primary crystallite formed at T_c, and the high melt peak reflected the melting of the relatively perfect lamellar stacks, resulting from recrystallization.[17] The corresponding melting temperatures (T_{mL} and T_{mH}) both increased with the molecular weight. T_{mH} reached 155°C at an M_n of 10,000.

As previously reported, ordinary PLLA was also crystallizable. The DSC curves and thermal transition characteristics of PLLA2 are also listed in Figure 2 and Table II, respectively. PLLA2 had a lower cold crystallization temperature but a higher T_m and crystallinity compared to dcPLLA with the same molecular weight (dcPLLA5). This indicated that dcPLLA had a slightly lower crystallizability compared to ordinary PLLA. The subtle distinction in chain structure, that is, the presence of the succinate moiety and two terminal carboxyl groups in the dcPLLA chain, may have been responsible for the difference.

However, dcPLLA had the same crystal structure as ordinary PLLA. Figure 3 illustrates the WAXD patterns of ordinary and dcPLLA samples after crystallization at 130°C. The diffraction peaks appearing at 2θ's of 12.4, 14.8, 16.7, 19.1, and 22.3° were assigned to the reflections of the 103, 010/104, 200/110, 203/014, and 210 planes, respectively. The diffraction peaks agreed well with the orthorhombic (α-form) crystal structure of PLLA, which has been extensively covered in the literature.[18–21]

T_g of dcPLLA also increased with its molecular weight because of the well-known dependence of free volume on the amount of chain ends. The molecular weight dependence of T_g (from the second heating scan) is plotted in Figure 4. T_g at infinite molecular weight was 56.6°C. It was very close to the

TABLE II
Thermal Transition Characteristics Acquired from the First Heating Scans of the dcPLLAs with Various Molecular Weights and PLLA2

| Sample	T_g (°C)	T_c (°C)	T_{mL} (°C)	T_{mH} (°C)	Crystallinity (%)
dcPLLA1	12.9/30.4	nd/nd	95.5/nd	109.0/nd	25.7/0
dcPLLA2	36.0/43.6	92.1/n	~118/n	133.7/138.3	25.1/0.5
dcPLLA3	41.6/48.2	99.5/112.8	128.7/133.0	146.4/146.2	36.5/27.4
dcPLLA4	51.0/51.8	104.1/110.9	135.0/136.0	149.6/148.8	39.8/36.2
dcPLLA5	51.5/52.7	107.1/114.0	142.7/143.6	154.6/154.7	39.6/40.2
PLLA2	52.4/45.1	96.7/105.9	nd/149.6	160.8/159.4	46.3/46.0

nd, not detected.
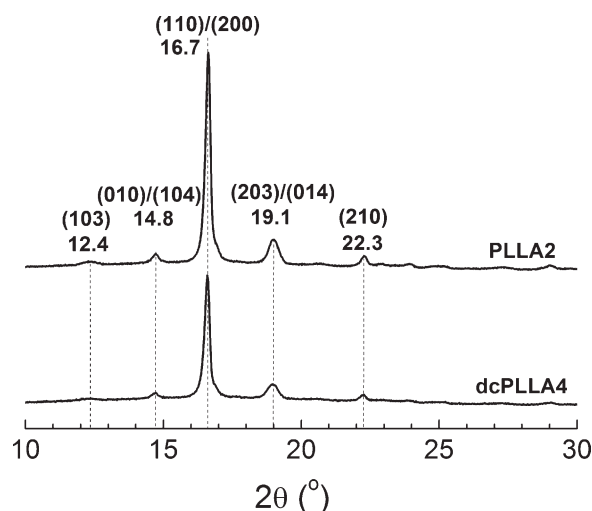
Figure 3 WAXD patterns of ordinary PLLA (PLLA2) and dcPLLA (dcPLLA4) after crystallization at 130°C.

widely reported values of 55–60°C for PLLA. Moreover, the T_g's were clearly higher than those of the amorphous dcPLLA reported in ref. 10, as compared in Figure 4. T_g at infinite molecular weight was 47.6°C for the amorphous dcPLLA. The higher T_g's of our dcPLLAs were mainly attributed to their crystalline natures. The crystalline chain in the crystallized dcPLLA sample impeded the movement of the amorphous chains and, therefore, raised its T_g. The shorter $(CH_2)_n$ moiety derived from anhydride or diacid (where n was 2 in this study and n was 4 in ref. 10) may also have had a slight contribution in raising T_g.

CONCLUSIONS

Crystalline dcPLLAs with M_n's of 10^3–10^4 g/mol were successfully synthesized via the melt
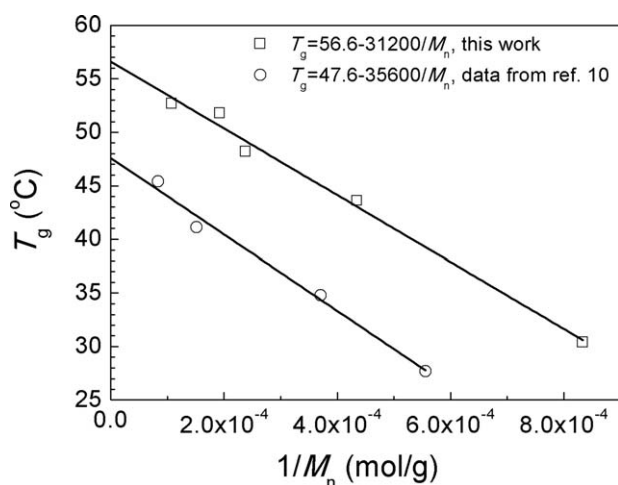
Figure 4 Dependences of T_g on M_n of dcPLLA in this study and in the study reported in ref. 10.

polycondensation of LLA in the presence of SAD with $SnCl_2$/TSA as a binary catalyst. The terminal COOH percentage reached as high as 98%, and the molecular weight was well controlled by the molar ratio of LLA to SAD. The molecular weight exhibited by dcPLLA depended the thermal transition behaviors. dcPLLA crystallized slowly at $M_n \leq$ 2000 but facilely at $M_n \geq 4000$. The crystallinity increased from 27 to 40% when M_n grew from 4000 to 10,000. In comparison to ordinary PLLA, dcPLLA had the same crystallization structure but a slightly lower crystallizability because of the subtle distinction in the chain structure. In addition, the crystalline dcPLLAs exhibited higher T_g values than the amorphous ones reported in the literature. The controllable molecular weight, high terminal COOH percentage, and high crystallinity make the dcPLLAs with $M_n \geq 4000$ suitable prepolymers for the synthesis of high-molecular-weight PLLA via chain extension. Further results will be reported later.

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