

Preparation and Characterization of High-Molecular-Weight Poly(L-lactic acid) by Chain-Extending Reaction with Phosphites

Ji-Xing Xie,^{1,2} Rong-Jie Yang¹

¹School of Materials, Beijing Institute of Technology, Beijing 100081, China

²College of Chemistry and Environment Science, Hebei University, Baoding 071002, China

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ABSTRACT: Poly(L-lactic acid) (PLLA) of high molecular weight was prepared by a chain-extending reaction in a microcompounder. Phosphites were used as chain extenders to increase the molecular weight of the PLLA prepolymer, which was prepared by the bulk polycondensation of L-lactic acid. The effects of the amount of phosphite, the temperature, and the screw speed on the torque of the PLLA melt were studied. Under the optimal conditions, the molecular weight of PLLA increased from 62,100 to 126,000 g/mol. The chemical structure and crystallinity of PLLA

were characterized by Fourier transform infrared spectroscopy, ¹H-NMR and ¹³C-NMR, differential scanning calorimetry, and X-ray diffraction. The mechanical properties of PLLA were measured. The results indicate that triphenyl phosphite (TPPi) was an effective chain extender for PLLA. The role of the TPPi in chain extending is suggested to be an esterification-promotion agent. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 124: 3963–3970, 2012

Key words: biodegradable; polyesters; reactive extrusion

INTRODUCTION

Poly(L-lactic acid) (PLLA) is a biobased and biodegradable polyester, which is increasingly used in the medical and industrial fields. In most applications, PLLA of high molecular weight (>100,000 g/mol) is demanded. High-molecular-weight PLLA is generally prepared by the ring-opening polymerization of the lactide,¹ whereas the lactide is produced by an oligomer of the lactic acid. Another way to yield PLLA of high molecular weight is the solution polycondensation of L-lactic acid (LLA).² It is difficult to reach a high-molecular-weight PLLA by the direct bulk polycondensation of LLA because of the unfavorable reaction equilibrium.³ Moon et al.,⁴ who examined the melt polycondensation of LLA catalyzed by a tin chloride dihydrate/*p*-toluene sulfonic acid (TSA) binary system, obtained PLLA of high molecular weight after 20 h with a yield of 67%. Recently, Chen et al.⁵ prepared high-molecular-weight PLLA by using titanium(IV) butoxide as a catalyst after 40 h. Lei et al.⁶ took the caprolactam and tin(II) chloride dihydrate (SnCl₂·2H₂O) as cata-

lysts and obtained poly(lactic acid) with a molecular weight of 50,000 and a yield of 87–94% after 16 h.

Chain extenders, such as ethylene carbonate, heterocyclic compounds, and diisocyanates, have been used to increase the molecular weight of the PLLA.⁷ However, these chain extenders change the chain structure of the PLLA. Triphenyl phosphite (TPPi), as a chain extender, has been used to increase the viscosity of poly(ethylene terephthalate) (PET) and poly(butylene terephthalate), whereas the chain structures of PET and poly(butylene terephthalate) could be maintained.^{8,9} The reactive extrusion process is a very attractive approach for the preparation of high-molecular-weight PLLA. Jacobsen et al.¹⁰ studied the polymerization of lactide in a twin-screw extruder and obtained PLLA with a molecular weight of 100,000 after 7 min.

In this study, phosphites were used in the chain extension of PLLA prepolymer through reactive extrusion in a twin-screw microcompounder, and high-molecular-weight PLLA was obtained in a short time. The structures of PLLA were characterized, and the chain-extending mechanisms are discussed.

EXPERIMENTAL

Materials

LLA, as an 88 wt % aqueous solution, was purchased from Fengyuan Corp. (Fengyuan, China) SnCl₂·2H₂O and tin(II) octoate [Sn(Ot)₂] were

Correspondence to: R.-J. Yang (yrj@bit.edu.cn).

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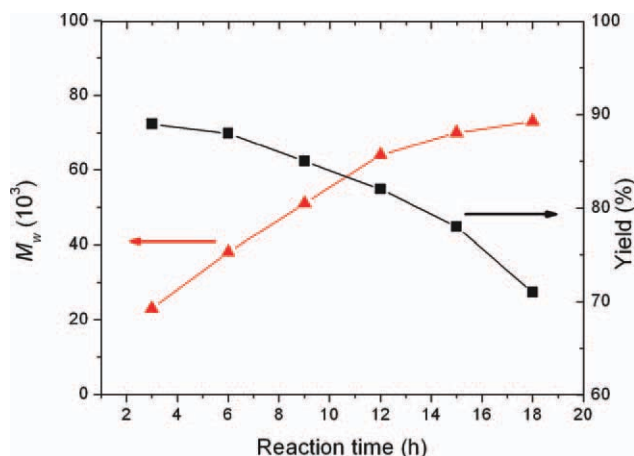


Figure 1 Variations of the molecular weight and yield as a function of the reaction time for the PLLA bulk polycondensation of lactic acid at 160°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

purchased from Beijing Chemical Corp. (Beijing, China) TSA, TPPi, trinonylatedphenyl phosphite (TNPi), and *trans*-(2,4-di-*tert*-butylphenyl) phosphite (TBPi) were purchased from Shanghai Chemical Corp. (Shanghai, China). All of these materials were used without further purification. The other chemicals were reagent grade.

Preparation of PLLA

The PLLA prepolymer was prepared through the bulk polycondensation of LLA with the combined catalysts $s\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Sn}(\text{Ot})_2$, and TSA in a flask reactor at 160°C. The PLLA prepolymer white powder was obtained after purification.

The prepolymer, which was dried at 60°C for 2 h, was mixed with certain amounts of the phosphite and then fed into the twin-screw microcompounder (Haake MiniLab) at a certain temperature. The feeding time was 5 min, and the residence time of the reactants was controlled in the range 0–30 min. The mixing reactants in the microcompounder were protected by a nitrogen atmosphere. Finally, the products were extruded from the die and molded by a mini-injection-molding machine connected to the microcompounder.

Characterizations

The average molecular weight and polydispersity of PLLA were determined by gel permeation chromatography (GPC; Waters 1515 HPLC pump with a Waters 2424 refractive-index detector, calibrated with polystyrene standards). Tetrahydrofuran was used as the eluent.

³¹P-NMR was recorded on a Bruker AV600 spectrometer with the external standard (85% H_3PO_4). ¹³C-NMR and ¹H-NMR spectra were obtained with

a Bruker DMX-400 NMR spectrometer with CDCl_3 as a solvent and tetramethylsilane (TMS) as an internal standard.

Fourier transform infrared (FTIR) analysis is carried out with a Nicolet 5DX spectrometer. The PLLA samples are pressed to pellet together with potassium bromide.

Differential scanning calorimetry (DSC) analysis was carried out on a TA Instruments Q100 from –20 to 200°C at a heating rate of 10°C/min under a nitrogen atmosphere.

X-ray diffraction (XRD) experiments were carried out with a Rigaku D/MAX-RA X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The scattering angle (2θ) was varied from 5 to 30°.

Measurement of the mechanical properties of PLLA was carried out with dog-bone specimens on a DXLL-5000 tensile testing machine at room temperature with a speed of 10 mm/min.

RESULTS AND DISCUSSION

Bulk polycondensation of PLLA

Figure 1 shows the effects of the reaction time on the molecular weight and the yield of PLLA in the bulk polycondensation of lactic acid in the flask reactor at 160°C. The molecular weight and the yield were varied in the opposite way with reaction time, and a cross point was observed at 11 h between the two curves of the molecular weight, and the yield in Figure 1 was at 11 h. The PLLA product at this time was designated as the prepolymer PLLA₀. The principal characteristics of PLLA₀ are listed in Table I. PLLA₀ was used in the reactive extrusion that followed.

Bulk polycondensation of lactic acid involves two thermodynamic equilibria: a dehydration/hydration equilibrium for ester formation and a ring/chain equilibrium for lactide formation. In the kinetics, the rate of dehydration decreased stepwise with increasing melt viscosity, whereas the rate of decomposition of the PLLA prepolymer increased. As a whole, the molecular weight of the PLLA prepolymer increased with the reaction time and finally reached a plateau.¹¹

Reactive extrusion of PLLA

The twin-screw microcompounder was taken as a reactor to realize the further polycondensation of

TABLE I
Main Characteristics of PLLA₀

M_n (g/mol)	M_w (g/mol)	M_w/M_n	Color	Acid value
86,700	62,100	1.54	White powder	1.5

M_n = Viscosity-average Molecular Weight.

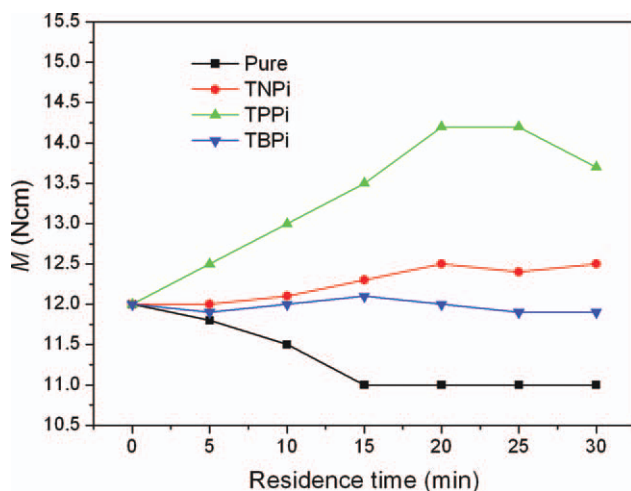


Figure 2 Torque values of the PLLA melts as a function of the residence time in the compounding process for different 1% phosphites at 160°C and 60 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PLLA₀ at a certain temperature. The residence time of the PLLA melt in the compounder could be controlled through its circumfluence.

As shown in Figure 2, for the pure PLLA₀, the melt torque (M) in the compounder decreased with increasing residence time at 160°C. This indicated that the PLLA was prone to degradation in the compounding process at the melting state. A similar relationship between the melt torque and molecular weight of PET was observed by Jacques et al.¹²

Effect of phosphite

Three kinds of phosphites (1.0 wt %) were added to PLLA₀ to inhibit the degradation of PLLA during the compounding process. As shown in Figure 2, the addition of TPPi made the melt torque increase quickly and reach a maximum at a residence time of 20 min, which means that the TPPi greatly increased the viscosity of the PLLA melt. TNPi made the torque rise slightly with residence time; TBPi kept the torque values unchanged. This means that the addition of TPPi obviously increased the viscosity of the PLLA melt, that is, the molecular weight of PLLA, whereas TNPi did it to a certain extent.

Because the degradation of PLLA was inevitable, the increase of the melt torque should have been attributed to the chain-extending reactions of the PLLA with the phosphites. In the phosphites, TPPi was the most prominent in the chain extension. Nevertheless, when the residue time was over 20 min, the melt torque decreased with TPPi added, which indicated the dominant degradation of PLLA after the complete consumption of the TPPi.

Effect of temperature

Figure 3 shows a comparison between two curves of the melt torque versus the residence time at 160 and 180°C with TPPi added. The torques at 180°C were lower than that at 160°C, especially when the residence time was over 20 min. It seems that a high temperature was not helpful in accelerating the chain extension of PLLA by TPPi but resulted in a larger degradation.

Screw speed

Three screw speeds of 30, 60, and 90 rpm were brought to bear on the screw in the micro-compounder. The curves of the melt torques as a function of the residence time at 160°C are shown in Figure 4. The highest melt torque appeared at 20 min at the speed of 60 rpm. Although at the speed of 90 rpm the melt torque was high in the beginning, it decreased quickly after 15 min. This implies that the high screw speed led to PLLA degradation because of the strong shearing involved.

Amount of TPPi

The variations in the melt torque at 160°C with respect to the amount of the TPPi are shown in Figure 5. TPPi at 1.0, 2.0, and 5.0 wt % induced a large increase in the melt torque in mixing compared to the pure PLLA. Nevertheless, the torque with the TPPi at 5.0 wt % was lower than that at 2.0 wt %. This indicates that a large amount of TPPi was not advantageous to the chain-extending reaction of PLLA.

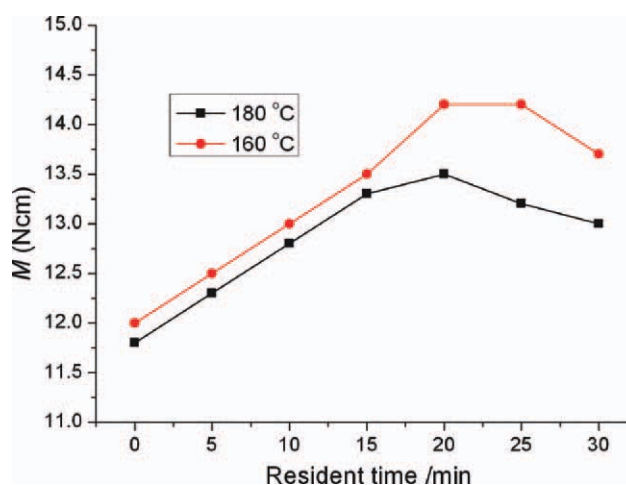


Figure 3 Torque values of the PLLA melts as a function of the residence time in the compounding process at 160 and 180°C for PLLA-1% TPPi at 60 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

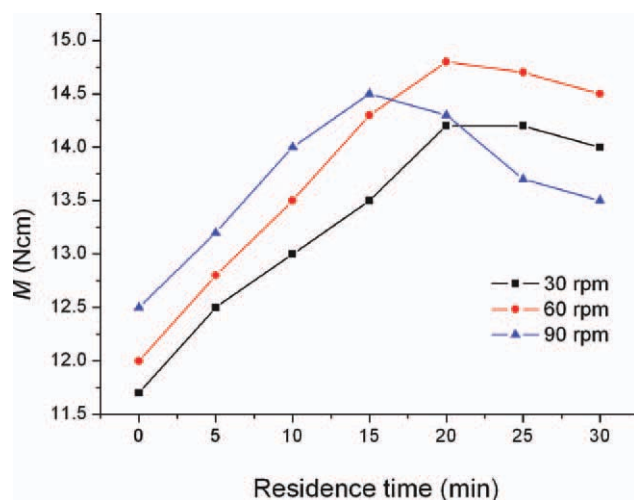


Figure 4 Torque values of the PLLA melts as a function of the residence time in the compounding process at 30, 60, and 90 rpm for PLLA-1% TPPi at 160°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The molecular weights of the PLLA product at the maximum torque are listed in Table II. The weight-average molecular weight (M_w) of the PLLA increased with the addition of TPPi; at the same time, the polydispersity of the molecular weight broadened. When the TPPi was at 2.0 wt %, the largest M_w was reached; this was consistent with the highest torque obtained, as shown in Figure 5.

The chain-extending reaction of PLLA should have taken place on the end hydroxyl groups. The calculated molar ratios of TPPi/OH groups in the reactive system are listed in Table I. When the molar ratio of TPPi to OH was too high, the TPPi could

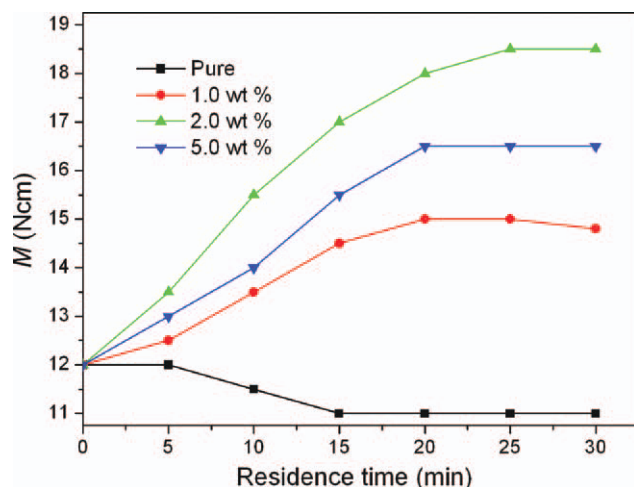


Figure 5 Torque values of the PLLA melts as a function of the residence time in the compounding process at 160°C for PLLA₀, PLLA-1% TPPi, PLLA-2% TPPi, and PLLA-5% TPPi at 60 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
PLLA Molecular Weights Determined by GPC as a Function of TPPi Content

Sample	Amount of TPPi (wt %)	TPPi/OH molar ratio ^a	GPC	
			M_w (g/mol)	M_w/M_n
PLLA-TPPi	1.0	0.96	93,000	1.60
	2.0	1.92	126,000	1.69
	5.0	4.80	102,000	1.72

M_n = number-average molecular weight.

^a Number of end OH groups in PLLA₀ determined by titrimetric method with a supposition that the number of end OH groups is equal to that of the end COOH groups.

react with the end carboxyl group, which was disadvantageous to PLLA chain extension. That is why the PLLA with 5.0 wt % TPPi had a lower M_w than that with 2.0 wt % TPPi.

Structure characterization of PLLA

Figure 6 shows the FTIR spectra of the PLLA₀ and PLLA-TPPi (2.0 wt %). They had similar infrared absorbance peaks except for small peaks at 1600 and 2110 cm^{-1} and a little difference in the relative intensities for several absorbance peaks. The absorbance at 1600 cm^{-1} belonged to stretching vibration of the phenyl group; the one at 2110 cm^{-1} was correlated with the stretching vibration of the P-H group.

Figure 7 shows the ¹H-NMR spectra of the PLLA₀ and PLLA-TPPi. For PLLA₀, only two peaks were observed at the chemical shifts at 1.5 and 5.2 ppm (the peak at 7.3 ppm was for the solvent). For PLLA-TPPi, small new peaks appeared at 4.3, 6.8, and 6.9 ppm, and the peaks at 1.5 and 5.2 ppm broadened. The peak at 4.3 ppm was attributed to

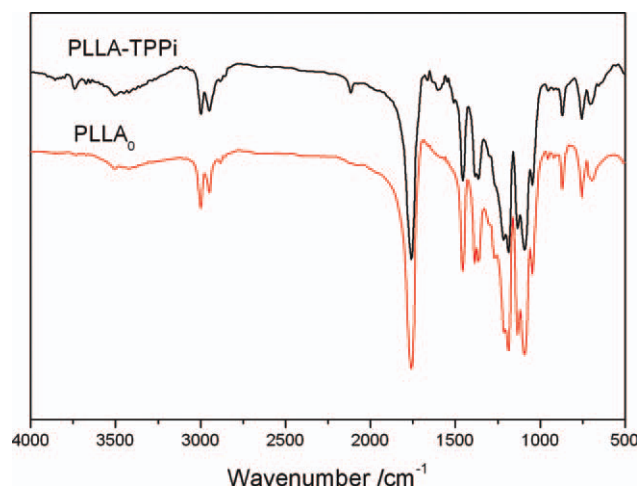


Figure 6 FTIR spectra of PLLA₀ and PLLA-2% TPPi. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

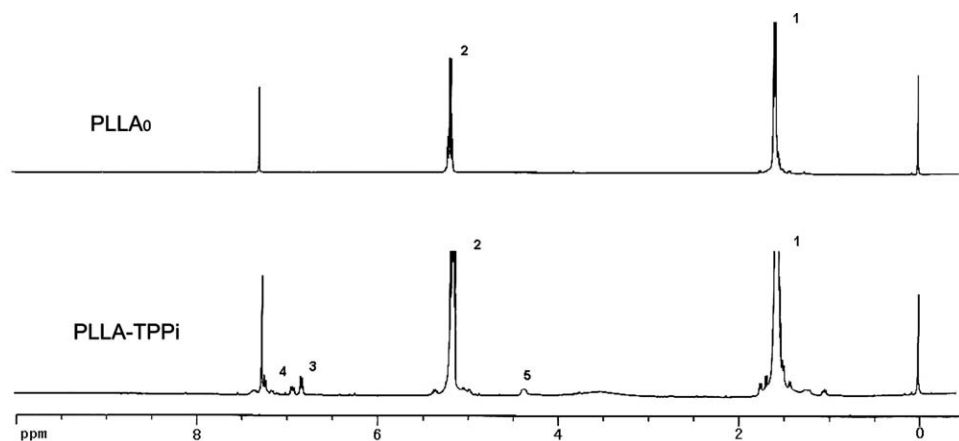


Figure 7 ^1H -NMR spectra of PLLA₀ and PLLA-2% TPPi.

the methine in the end groups, and those at 6.8 and 6.9 ppm corresponded to the phenyl proton induced by TPPi. The broadening peaks at 1.5 and 5.2 ppm indicated the existence of PLLA of low molecular weight in the final product.

In the ^{13}C -NMR spectra of PLLA-TPPi, as shown in Figure 8, there were only three signals at chemical shifts of 169.7, 69.0, and 16.6 ppm. The signal at 169.7 ppm was rather sharp, as shown in its magnification. According to Mark et al.,¹³ the single sharp peak indicated that the chain configuration of PLLA was in uniform L-type lactic acid units with few D-type units. In other words, the racemization of the L-type units was not evident during the polycondensation of the LLA.

DSC and XRD analysis

The thermal behaviors of PLLA₀ and PLLA-TPPi were studied through DSC. Figure 9 shows the DSC

curves of the two samples. In the curves, there were three thermal processes: glass transition with glass transition temperature T_g , crystallization with crystallization temperature T_c , and crystal melting with melting temperature T_m . T_g of PLLA-TPPi (2.0 wt % TPPi) was 49.4°C and was lower than that of PLLA₀, as listed in Table II, which should have correlated with the plasticization of the organic phosphorus compounds and the broadening polydispersity of PLLA-TPPi.

The cold crystallization process of PLLA₀ caused a mild exothermic peak at about 125°C, whereas the process of the PLLA-TPPi caused a sharp exothermic peak at 100°C, which indicates that the PLLA-TPPi began to crystallize faster and earlier than the PLLA₀. The PLLA-TPPi and PLLA₀ showed similar melting processes at 149°C, which corresponded to the α crystal, but the PLLA-TPPi had another small melting peak at 135°C, which corresponded to the β crystal. The calculated degree of crystallization (X_c)

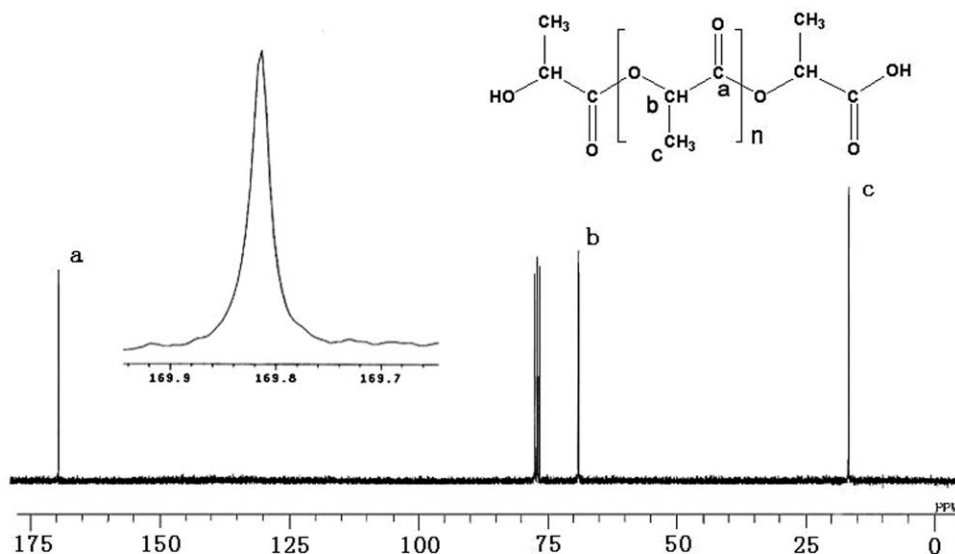


Figure 8 ^{13}C -NMR spectra of PLLA-TPPi (2.0 wt %).

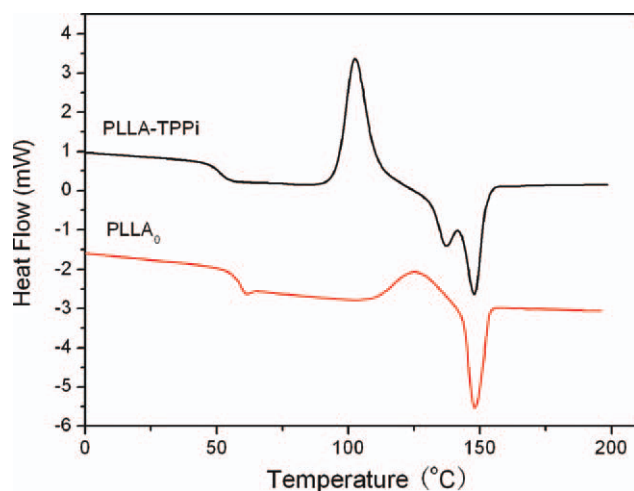


Figure 9 DSC thermograms of PLLA₀ and PLLA-2% TPPi. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the PLLA-TPPi, as listed in Table III, was 33.9% and was lower than that of PLLA₀. X_c was determined by division of the endothermic amount of the melting peak by the melting heat of 93.6 J/g for 100% crystalline PLLA.¹⁴

Figure 10 shows the XRD patterns of the PLLA-TPPi and PLLA₀. PLLA₀ had the sharpest peak at 16.7° (2θ , 020 reflection) and small peaks at 14.8° (101 reflection) and 19.1° (023 reflection), respectively. The PLLA-TPPi showed similar but a little weak diffraction peaks at the same 2θ , which correlated with a low degree of crystallinity of the PLLA-TPPi.

Mechanical properties

The mechanical properties of the PLLA₀ and PLLA-TPPi are listed in Table II. PLLA₀ had very poor mechanical properties because of its low molecular weight. The mechanical properties of the PLLA-TPPi improved greatly because of the increase in the molecular weight through chain extension by TPPi. The tensile strength of PLLA-TPPi reached 63 MPa and was comparable with the commercial PLLA commonly prepared by the open-cycle polymerization of the lactide.

Chain-extending mechanism by phosphite

Figure 11 shows the ³¹P-NMR spectra of the initial mixture of PLLA₀ and TPPi (2.0 wt % TPPi) and the

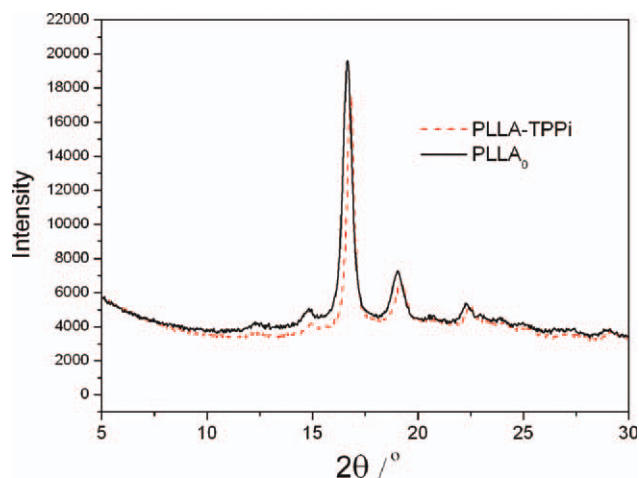


Figure 10 Wide-angle X-ray diffraction diffractograms of PLLA₀ and PLLA-2% TPPi. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

final PLLA-TPPi product at the residence time of 30 min in the microcompounder. For the initial mixture, the peak at 131 ppm belonged to the triphenyl phosphite (TPPi, P(OC₆H₅)₃) P(OR)₃ of the TPPi, the small peaks at 0–5 ppm corresponded to impurity in the TPPi. For the final PLLA-TPPi product, the peak at 131 ppm disappeared, and the peaks at 0–8 ppm became stronger. The resonance peaks at 0–8 ppm were attributed to the phosphorus atoms bonded to hydrogen (P–H).¹⁵

The absorbance peak at 2110 cm⁻¹ in the FTIR spectra in Figure 6 can be considered as more evidence of the P–H group.

The peak at 4.3 ppm in the ¹H-NMR spectra in Figure 7, attributed to the methine in the chain end, means that there was the ending of the –CH₂–O–P(OC₆H₅)₂ group.

The chain-extending effect of TPPi for PET has been studied.^{16,17} Like the PET, PLLA has both hydroxyl and carboxyl end groups. We expected that PLLA would have a similar chain-extending mechanism by TPPi as for PET, as shown in Scheme 1.

TPPi could react with the –OH group of PLLA first and form PLLA of the ending diphenyl phosphite [PLLA–O–P(OC₆H₅)₂]. The ending –O–P(OC₆H₅)₂ group reacted with the end –OH or –COOH of another PLLA molecule to extend the chain and release HO–P(OC₆H₅)₂ at the same time. In other words, the phosphite just promoted the esterification between the end groups of PLLA. If

TABLE III
Thermal and Mechanical Properties of PLLA₀ and PLLA-TPPi

Sample	T_g (°C)	T_c (°C)	T_m (°C)	X_c (%)	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)
PLLA ₀	57.1	125	149	37.8	14	1.1	2.1
PLLA-TPPi	49.4	100	149, 135	33.9	63	2.3	4.5

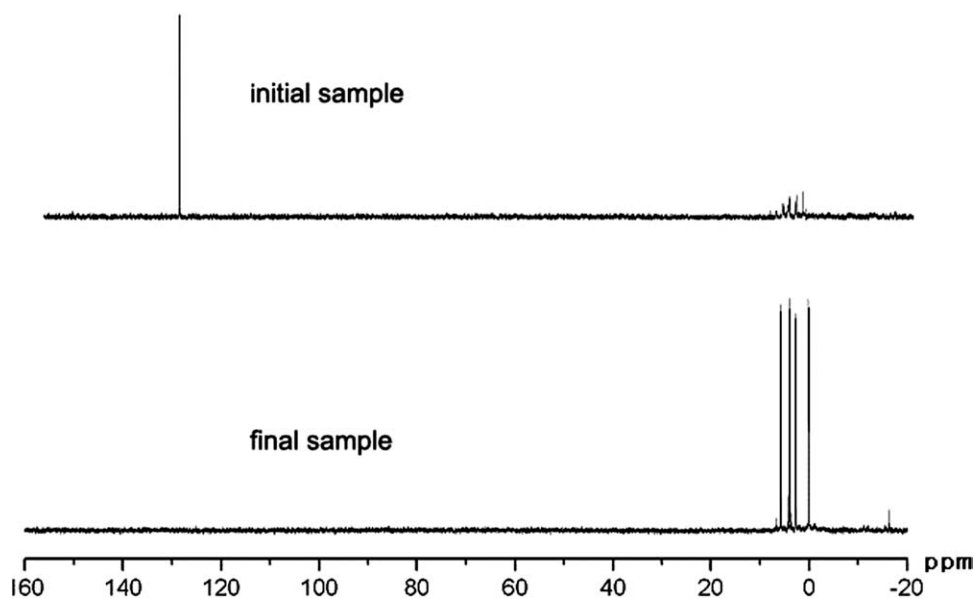


Figure 11 ^{31}P -NMR spectra of the mixture of the reactive PLLA-2% TPPi (residence time = 30 min) and the initial mixture PLLA₀+TPPi (residence time = 0 min).

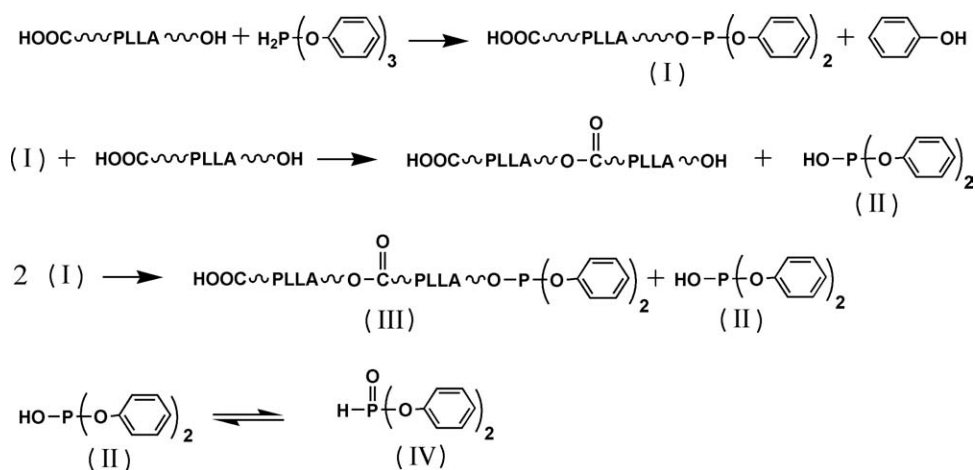
TPPi reacted with the end carboxyl group of PLLA, it would have formed a stable phenyl ester; this may have reduced the chain reaction. The isomer of the $\text{HO}-\text{P}(\text{OC}_6\text{H}_5)_2$ may have transferred to $\text{H}-\text{P}=\text{O}(\text{OC}_6\text{H}_5)_2$ each other, which may have explained existence of P-H in the ^{31}P -NMR spectra.

In addition, TPPi might have reacted with water in the system, which would have been favorable to the polycondensation of PLLA.

CONCLUSIONS

PLLA of high molecular weight ($M_w = 126,000$ g/mol) was prepared through chain-extending reactions by the phosphites in a twin-screw microcompounder. Among the three kinds of the phosphites (TPPi, TNPi, and TBPi), TPPi was the best

chain extender of PLLA. The melt torque of pure PLLA in the compounding decreased with the residence time; with TPPi added, the melt torque first increased and went through the maximum and finally decreased with the residence time. These indicated that there were competitive extending and degradation reactions of the PLLA chains. The presence of the TPPi could have made the polycondensation of the PLLA continue and inhibit the degradation of PLLA to a certain extent. The optimal amount of TPPi under the experimental conditions was around 2.0 wt % to achieve PLLA of high molecular weight. PLLA with TPPi added showed low T_g and low X_c but an evidently high tensile strength compared to the pure PLLA. The chain-extending mechanism of TPPi for the PLLA is considered to be an esterification promoter.



Scheme 1 Chain-extending reaction of PLLA by TPPi.

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