Polym. Bull. (2011) 66:315–326
DOI 10.1007/s00289-010-0280-3

ORIGINAL PAPER

# Synthesis, characterization of star-shaped copolymers of L-lactide and epoxidized soybean oil

**Jun Zou · Xuan Chen · You Shu · Haijun Zhou · Farong Huang**

Received: 8 October 2009 / Revised: 27 March 2010 / Accepted: 29 April 2010 /

**Abstract** Biodegradable star-shaped PLLA–ESO copolymers were synthesized by the bulk copolymerization of L-lactide (L-LA) and epoxidized soybean oil (ESO) with stannous octanoate as the catalyst. Effects of molar ratios of monomer to catalyst, and various amounts of ESO on copolymerization were studied. The resulting copolymers were characterized by FTIR, $^1$H NMR, GPC, etc., which confirmed the successful synthesis of star-shaped copolymers of L-LA and ESO. The thermal and mechanical properties of samples were also investigated by means of DSC, TGA and tensile testing. The results showed that the PLLA–ESO copolymers possed lower glass transition temperature, melting point, crystallinity, and maximum decomposition temperature than those of neat polylactide. Tensile testing demonstrated that PLLA–ESO copolymer had better ductility than linear PLLA. It was also found that the amount of catalyst almost had no influence on the weight average molecular weight of PLLA–ESO copolymers, but which could be controlled by variation of molar ratios of L-LA to ESO.

**Keywords** L-lactide · Epoxidized soybean oil · Star-shaped copolymer · Thermal stability

---

J. Zou · F. Huang (✉)
Key Laboratory for Specially Functional Polymeric Materials and Related Technology of the Ministry of Education, School of Materials Science and Engineering,
East China University of Science and Technology, Shanghai 200237,
People's Republic of China
e-mail: fhuanglab@ecust.edu.cn

J. Zou
e-mail: zj_881996@yahoo.com.cn

J. Zou · X. Chen · Y. Shu · H. Zhou
School of Materials Science and Engineering, JiangSu University of Science and Technology,
Zhenjiang 212003, Jiangsu, People's Republic of China

## Introduction

Poly(L-lactide)s (PLLA) are biodegradable polymer resins derived from annually renewable resources [1]. With good biodegradability, high mechanical strength, and excellent shaping and molding properties, PLLA was regarded as one of the most promising biodegradable polymers and was expected to substitute some of the non-biodegradable plastics [2, 3]. Although PLLA is a high-strength and high modulus polymer analogous to polystyrene, it has inherent brittleness and low toughness [3, 4] which restrict the range of applications. Under tension, polylactide fractures at very low strains (ca. 3%), and is therefore unsuitable for use in numerous applications where elasticity and ductility are essential. Meanwhile, PLLA suffers from the induction of material defects based on lability of melt viscosity.

Modifications of polylactide such as blending PLA with immiscible or miscible polymers [4–7] can be used to enhance its physical properties, thus widening its applicability. PLLA has been blended with a number of different polymers, e.g. poly(butylene adipate-co-terephthalate), poly(3-hydroxy butyrate), poly(3-caprolactone), poly(vinyl acetate), poly(methyl methacrylate), poly(ethylene oxide), polystyrene and polyethylene. However, most of the polymer blends are immiscible, and the multiphase blends show poor mechanical performance because of the low interfacial adhesion between the polymer phases. The promising approaches to overcome these problems are the introduction of units to control the biodegradability and branched structure to improve elasticity, ductility and/or stabilize the melt viscosity in PLLA.

Fumitaka Tasaka et al. reported the synthesis of novel comb-type polylactide and revealed that the controlled degradation and good molding properties of comb-type polylactide. Meanwhile, star-shaped polymers, block polymers, hyperbranched and dendritic polymers [8–19] have been attracting much attention due to their various functions and properties resulting from their special three-dimensional structures. Among them, increasingly importance has been attached to star-shaped polymers. Up to now, the synthesis of star-shaped polylactides and poly(lactide-co-glycolide)s with multifunctional initiators, such as glycerol [20, 21], pentaerythritol [22], mannitol/sorbitol [23], aminopropanediol or aminohydroxy methylpropanediol [24] and stannous octoateatalyst have been investigated.

Epoxidized soybean oil (ESO) is epoxidized glycerol fatty esters. It originates from a renewable resource and therefore is biodegradable. The epoxy functionality provides excellent heat and light stability. ESO has been used as plasticizer and stabilizer in plastic materials to keep plastics and rubber soft and pliable. Recently, Fathilah Ali [25] reported the thermal, mechanical and rheological properties of poly(lacitic acid)/epoxided soybean oil blends, Choi [26] reported that ESO is an effective plasticizer for a biodegradable bacterially synthesized poly(3-hydroxybutyrate-co-3-hydroxyvale-rate) by depressing glass transition temperature as well as increasing elongation at break and impact strength of the polymer.

Though the flexibility of PLLA could be temporarily achieved by incorporating ESO using melt blending, however, PLLA is a kind of semi-crystalline polymer, after a period of time, the non-crystalline part of the material will gradually crystallize, ESO easily precipitate on the surface of the PLLA. Due to biodegradability, its inherent resistance to oxidation, and long chain segment of $-CH_2-$ of ESO, it would be beneficial to the copolymerization of L-LA and ESO, furthermore, permanently enhance the elasticity and ductility of PLLA.

In this article, star-shaped copolymers of L-lactide (L-LA) and epoxidized soybean oil in the presence of stannous octoate ($SnOct_2$) were synthesized. Effects of molar ratios of L-LA to epoxidized soybean oil and monomer to catalyst on the molecular weight of copolymer were studied. In addition, the thermal and mechanical properties of the synthesized star-shaped copolymers were also investigated.

## Experimental

### Materials

L-lactide was synthesized according to the literature [27], and purified by recrystallization using dry toluene and ethyl acetate as solvent epoxidized soybean oil (ESO, epoxide content = 6.9 wt%) was procured from Shindongbang Co, Korea.

Prior to copolymerization, both the L-LA and ESO were dried overnight at 50 °C in vacuum. Stannous octanoate (Sigma, A. R.) was used as received. Dichloromethane and methanol were used as received.

### Preparation of samples

Certain amounts of L-LA, ESO and $SnOct_2$ were accurately weighed and placed into a dried flask, which was silanized beforehand. The flask was purged thrice with dry argon and sealed after evacuation. Under stirring, the flask was immersed in an oil bath at 160 °C for 5 h. The obtained raw product was purified by dissolution in dichloromethane and re-precipitation by methanol, followed by vaccum drying at 60 °C until it reached a constant weight.

### Characterization

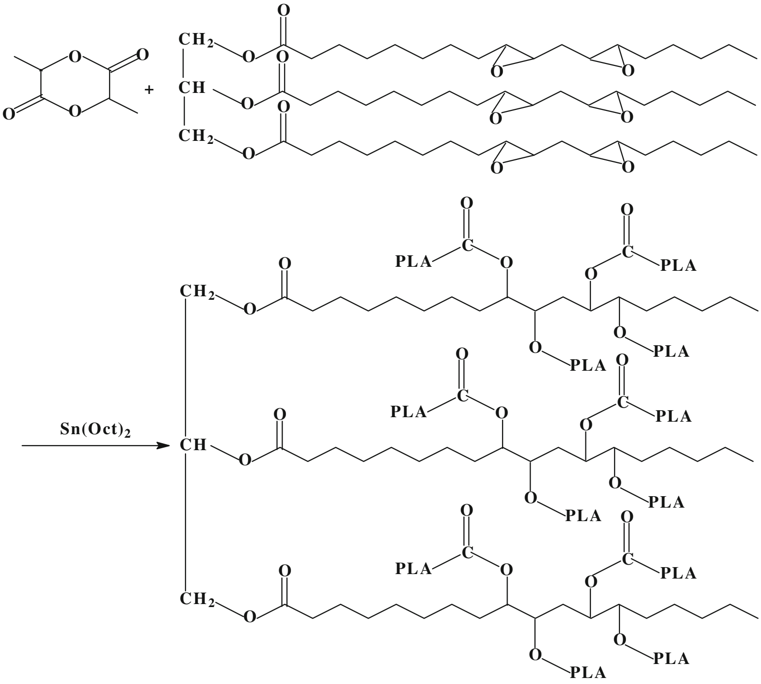
FTIR spectroscopic analyses were performed on a Perkin-Elmer 2000 spectrometer with KBr discs. $^1H$ NMR spectroscopy were carried out with a Bruker DMX 400 spectromer. $CDCl_3$ was used as the solvent for the $^1H$ NMR measurements. The GPC measurements were carried out at 35 °C with tetrahydrofuran (THF) as the eluent (1 ml/min) using a Waters 510 type pump and Shedox GPC KE 800 columns in series. Calibration was effected with polystyrene standards with a narrow molecular weight distribution. Molecular weights were determined according to the universal calibration principle. Differential scanning calorimetric analysis (DSC) was carried out on a Perkin-Elmer DSC7 series thermal analysis system, relative to indium standards, Samples of the copolymers (10 mg) were heated to 200 °C at a rate of 10 °C/min. The samples were then quenched to $-100$ °C and subjected to a second run at the rate of 10 °C/min. The thermal stability of the samples (about 7 mg) was investigated with a TGA (TA-Q600) under nitrogen and air from room temperature (about 20 °C) to 600 °C at a heating rate of 10 °C/min. Intrinsic viscosity of PLLA were measured in chloroform at 25 °C. Tensile properties were measured using a Universal testing machine (Instron-5566) at 25 °C at a crosshead speed of 5 mm/min according to ASTMD638.

## Results and discussion

### Synthesis and characterization of star-shaped PLLA–ESO copolymers and PLLA

#### *Synthesis of star-shaped PLLA–ESO copolymers and PLLA*

The epoxy bonds in ESO, whose structural formula is given in Scheme 1, can be easily broken and then combine with the –OH and –COOH to form the star-shaped PLLA–ESO copolymers. Figure 1 shows the FTIR spectra of the pure PLLA, ESO and PLLA–ESO copolymer samples. The peaks at about 1746 and 1182 cm$^{-1}$ which belong to the C=O stretching and C–O–C stretching of PLLA, respectively, are clearly visible in the IR spectra. The characterstic peak at 1161 and 1106 cm$^{-1}$ were attributed to the C–O–C asymmetric stretching vibration and symmetrical stretching vibration of ESO, respectively. The presence of peak in the FTIR spectra



Scheme 1 Synthesis of star-shaped PLLA–ESO copolymer

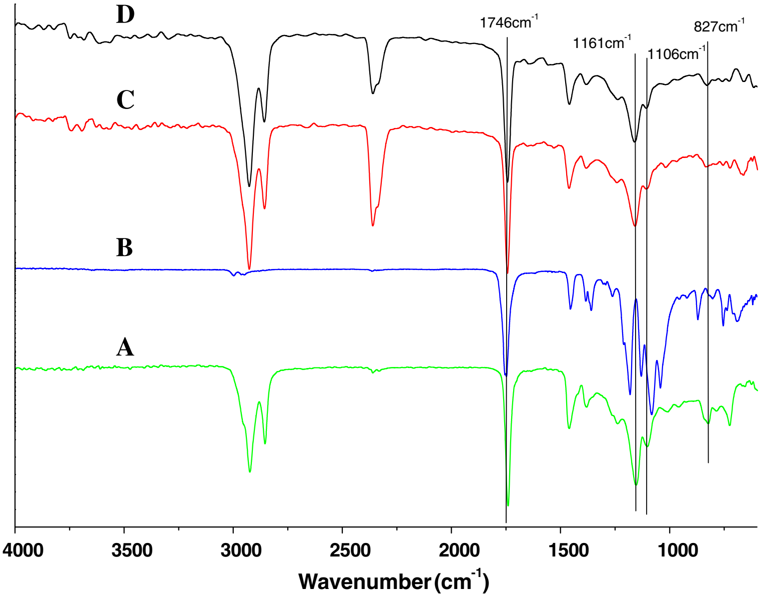


**Fig. 1** FTIR spectra: *A*, ESO; *B*, neat PLLA; *C*, PLLA–ESO (700/4) copolymer; *D*, PLLA–ESO (700/8) copolymer

of ESO at 827 $cm^{-1}$ was attributed to epoxy group. After L-LA copolymerizing with ESO in the presence of $SnOct_2$, three new peaks appear at about 827 $cm^{-1}$ (C–O–C of ESO), 1161 and 1106 $cm^{-1}$ which can be observed in the spectra of 4% ESO/PLLA, 8% ESO/PLLA. The absorbance intensities of these three new peaks clearly confirm the chemical reaction between L-LA and ESO. Figure 2 shows the $^1H$ NMR spectra of neat PLLA and PLLA–ESO copolymer. It can be found from Fig. 2a that the signals of methyl protons of the neat PLLA at 1.591–1.609 ppm appeared, and signals of methylene protons ($\delta = 5.156$–$5.207$ ppm) of PLLA were discovered. $^1H$ of –$CH_3$– from PLLA resonates in $\delta = 1.591$ ppm and 1.609 ppm with equal proton signals in intensity, and the $^1H$ of –CH– from PLLA induced the four peaks between 5.516 ppm and 5.207 ppm, signal intensity rate of the four peaks is 1:3:3:1; furthermore, the peak area ratio of –$CH_3$– and –CH– from PLLA is 3.03:1.00. $^1H$ NMR spectrum validates the structure of the PLLA. From Fig. 2b, it can be observed that the signals of methyl protons ($\delta = 0.895$ ppm) and methylene ($\delta = 1.271$ ppm) of ESO appeared, signals of methylene protons ($\delta = 5.154$–$5.206$ ppm) and methyl protons ($\delta = 1.588$–$1.606$ ppm) of PLLA were also discovered. This indicates that the PLLA–ESO copolymers have formed due to the chemical reaction between L-LA and ESO.

### *Effect of various amounts of ESO on copolymerization*

To investigate the effect of various amounts of ESO on copolymerization, the ring-opening copolymerization of L-LA and ESO was carried out with $SnOct_2$ catalyst in

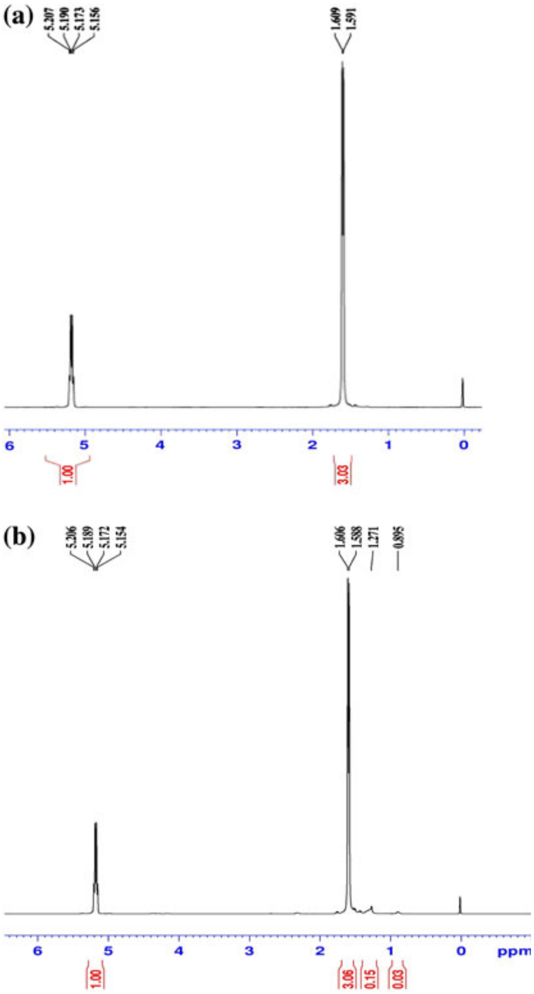


**Fig. 2** $^1$H NMR spectra of PLLA (**a**) and copolymer (**b**) of L-LA and ESO

bulk at 160 °C for 5 h. When various amounts of ESO were used, the results of copolymerization are shown in Table 1. Table 1 shows the relationship between the molecular weight and molar ratios of L-LA to ESO. From Table 1, it can be seen that the molecular weight distribution of the resulting copolymers of polylactides linearly increases with the molar ratio of L-LA to ESO. Meanwhile, it is noted that the weight average molecular weight attained maximum when the molar ratios of L-LA to ESO was 100/4, the results for the PLLA–ESO copolymers show a significant increase in the weight average molecular weight compared to PLLA, indicative of a coupling mechanism during the copolymerization. This is atrributed to the multiple oxirane functionality contained in most of the ESO molecules (an average of about 6.9 oxirane oxygens/molecule). However, the weight average molecular weight decreased when ESO percent in the monomers is more than 700/4, this may be due to the adverse effect on the PLLA–ESO copolymers chain

**Table 1** Effects of ESO molar ratios on molecular weight and molecular weight distribution of PLLA and PLLA–ESO copolymers

| Sample | [L-LA]/[ESO][a] | $M_n(10^4)$[b] | $M_w(10^4)$[c] | PDI | $[\eta]$/dL $g^{-1}$ |
|---|---|---|---|---|---|
| 1 | 0 | 5.81 | 6.82 | 1.17 | 0.650 |
| 2 | 700/1 | 5.33 | 8.22 | 1.54 | 0.721 |
| 3 | 700/2 | 5.99 | 9.41 | 1.57 | 0.753 |
| 4 | 700/4 | 6.68 | 11.93 | 1.79 | 0.752 |
| 5 | 700/5 | 6.44 | 11.77 | 1.83 | 0.717 |
| 6 | 700/8 | 5.26 | 10.41 | 1.98 | 0.705 |
| 7 | 700/10 | 3.59 | 7.22 | 2.01 | 0.665 |

Polymerization conditions: $SnOct_2$/L-LA(g/g) = 1:2000, 5 h at 160 °C

[a] Feed ratio of L-LA and ESO

[b] Determined by GPC analysis with polystyrene standards, THF was used as eluent

[c] $M_w$ from GPC measurement

propagation increased with the trace of peroxy-acid in ESO add up to a certain amount. As shown in Table 1, it can be found that the intrinsic viscosity of PLLA is less than that of PLLA–ESO copolymers under the same polymerization condition. The above results indicate that the PLLA–ESO copolymers are star-shaped copolymers, while PLLA is linear polymer. This is because the melt viscosity of linear PLLA is higher than that of star-shaped PLLA–ESO copolymers, which hindered the dehydration of polymerization and resulted in polymerization efficiency of linear PLLA significantly lower than that of PLLA–ESO copolymers.

## *Effect of $SnOct_2$ catalyst on polymerization*

Table 2 shows the influence of various amounts of monomer to catalyst. From Table 2, it can be found that the amount of $SnOct_2$ catalyst almost has no influence on the weight average molecular weight of the resulting polylactide copolymers. This also reveals that the epoxy bonds are the real initiator, which can stoichiometrically control the molecular weight of the star-shaped polymer. It is worth noting that with increasing concentrations of monomer to catalyst, the polymerization rate becomes slow, while the molecular weight distribution decreases. This can be attributed to the slow polymerization rate and the symmetry of the star-shaped polymer can be effectively controlled [22].

**Table 2** Results of copolymerization of L-LA and ESO with various amounts of $SnOct_2$ catalyst in bulk at 160 °C for 5 h

| Sample | [L-LA]/[ESO] | [L-LA]/[$SnOct_2$] | Conversion (%) | $M_n$ $(10^4)$ | $M_w$ $(10^4)$ | PDI |
|---|---|---|---|---|---|---|
| 8 | 700/5 | 2800/1 | 95.8 | 5.93 | 11.74 | 1.98 |
| 9 | 700/5 | 5600/1 | 91.5 | 6.44 | 11.78 | 1.83 |
| 10 | 700/5 | 8400/1 | 88.4 | 7.21 | 11.72 | 1.63 |
| 11 | 700/5 | 14000/1 | 81.7 | 8.49 | 11.92 | 1.40 |

**Table 3** Thermal properties of neat PLLA and PLLA–ESO copolymers determined by DSC

| Sample | $T_g$ (°) | $T_c$ (°) | $T_m$ (°) | $\Delta H_c$ (J/g) | $\Delta H_m$ (J/g) | $\chi_c$ (%) |
|---|---|---|---|---|---|---|
| 1 | 60.2 | 103.4 | 176.0 | 30.80 | 66.52 | 38.16 |
| 3 | 58.9 | 104.5 | 170.9 | 25.63 | 54.23 | 30.56 |
| 4 | 57.1 | 110.1 | 168.9 | 34.68 | 43.55 | 9.48 |
| 5 | 56.5 | 114.7 | 167.3 | 47.05 | 51.27 | 4.51 |
| 6 | 53.0 | 123.3 | 166.1 | 37.08 | 38.93 | 1.98 |

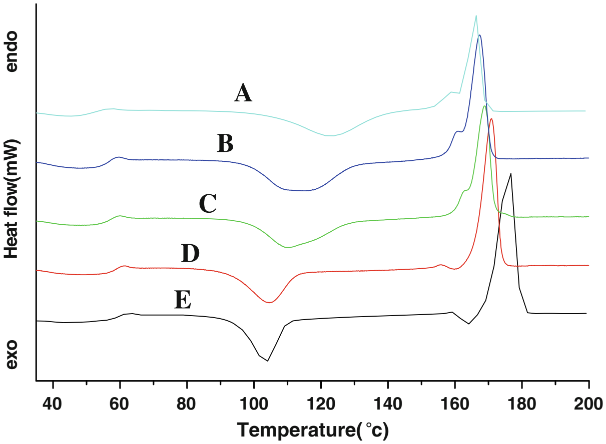


**Fig. 3** DSC heating curves of neat PLLA and PLLA–ESO copolymers, random: *A*, 700/8; *B*, 700/5; *C*, 700/4; *D*, 700/2; *E*, neat PLLA

## Thermal and mechanical properties of PLLA and PLLA–ESO copolymers

In this study, the thermal properties of star-shaped PLLA–ESO copolymers were investigated by DSC and TGA and compared with those of linear polylactide. The DSC and TGA results of star-shaped PLLA–ESO copolymers and linear polylactide are showed in Table 3, Figs. 3 and 4.

### *DSC analysis of PLLA and PLLA–ESO copolymers*

The crystallinity ($X_c$) of polylactides was determined from DSC measurements by the equation $\chi_c = (\Delta H_m - \Delta H_c)/\Delta H_m^0$; with the aid of the enthalpy of fusion of 93.6 J/g for the perfectly crystalline PLLA [28]. The various DSC parameters are summarized in Table 3. It is well known that the linear PLLA are semi-crystalline. As shown in Table 3, the polylactide copolymers possess lower melting points ($T_m$) and crystallinity than neat polylactide, which could be attributed to the crystalline imperfection mainly due to the short chain length of the star-shaped PLLA arms. Another important reason for the crystalline imperfection should be the branched structure of star-shaped PLLA–ESO copolymers. In the branched star-shaped,

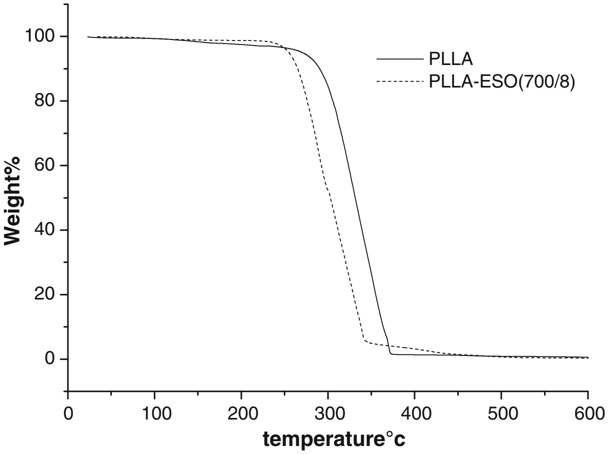


**Fig. 4** TGA curves of neat PLA and PLLA–ESO(700/8) copolymer samples under nitrogen

PLLA–ESO copolymers, the chains of PLLA were attached to a ESO core; therefore, chain movements were hindered and their crystallisability was weakened, whereas no such steric hindrance existed in linear PLLA. The $T_g$ decreased from 60.2 °C of neat PLLA to 53.0 °C of PLLA–ESO (700/8) copolymers, due to the introduction of methylene soft segment of ESO. The low melting point of polylactide copolymers obtained in the range of 166.1–170.9 °C can be attributed to the crystalline imperfections due to increased free end groups and branching points in the more branched polymers [14]. Meanwhile, it is noted that the star-shaped PLLA–ESO copolymers have two melting signals, which can be observed often in semi-crystalline polymers [29]. The phenomenon is resulting from the crystallinities of different sizes and different degrees of crystalline perfection. It can also be seen from Fig. 3 that the crystallization temperature ($T_c$) of PLLA gradually increased by the addition of ESO, which confirmed that ESO decreased the crystallizability of PLLA.

## *TGA analysis and mechanical properties of PLLA and PLLA–ESO copolymers*

The thermal stability of PLLA and PLLA–ESO (700/8) copolymer samples was determined by TGA under nitrogen and air. As shown in Fig. 4, the maximum decomposition temperature ($T_{max}$) of PLLA–ESO(700/8) copolymer is obviously lower than that of linear polylactide. As a comparison, the TGA thermograms of PLLA–ESO(700/8) copolymer and linear polylactide are outlined in Fig. 4. It can be observed that the PLLA–ESO copolymer and linear PLLA start to decompose at about 240 and 260 °C, respectively. The maximum decomposition temperature and the corresponding derivative weight of PLLA–ESO(700/8) copolymer are 261.3 °C and 1.52%. As for neat PLLA, the corresponding values of $T_{max}$ and the maximum derivative weight are 303.4 °C and 4.82%, respectively. The results indicate that the thermal stability of linear polylactide is excellent than that of PLLA–ESO

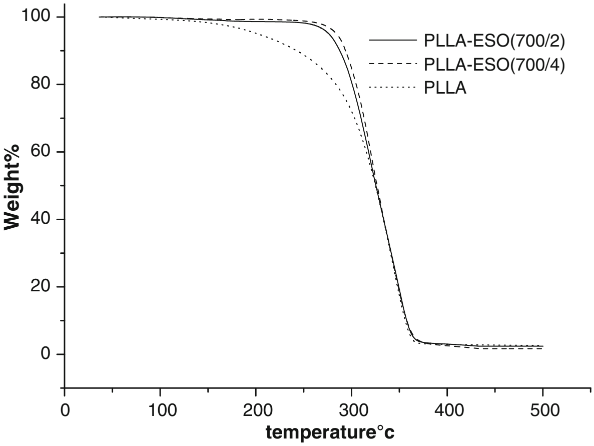


**Fig. 5** TGA curves of neat PLA and PLLA–ESO copolymer samples under air

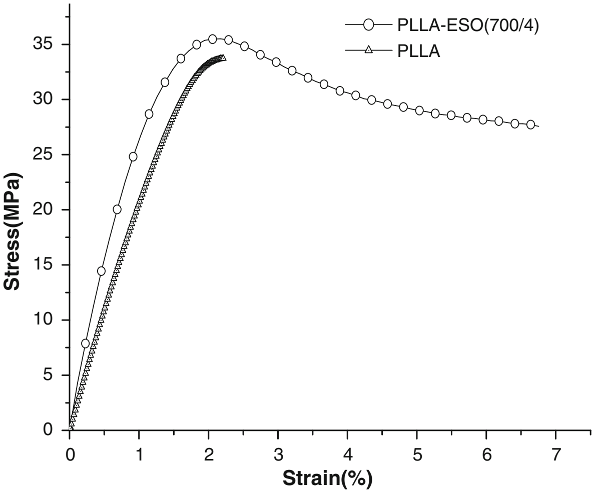


**Fig. 6** Stress–strain curves of neat PLLA and PLLA–ESO(700/4) copolymer

copolymer. The relatively poor thermal stability can be ascribed to the thermally unstable nature of hydroxylterminated polylactides, which are liable to decompose to form cyclic monomer [30]. Moreover, the weight loss of star-shaped PLLA–ESO copolymer was higher than that of corresponding linear PLLA, which should be ascribed to the much shorter polylactide chains in star-shaped PLLA–ESO.

The oxidation resistance of linear PLLA and PLLA–ESO copolymers have been investigated with TGA analysis under air. From Fig. 5, it can be seen easily that the maximum decomposition temperatures ($T_{\max}$) of star-shaped ones (Sample 2 and Sample 3) are higher than that of linear PLLA (Sample 1), indicating that the thermal stability of PLLA–ESO copolymers are better than that of linear PLLA.

Moreover, it has the tendency that the thermal stability of PLLA–ESO copolymers increased with the molar ratios of ESO increased, indicating the improvement of the oxidation resistance of PLLA–ESO copolymers. This may also be due to ESO with high heat resistance in the PLLA–ESO copolymers which improved the oxidation resistance (Fig. 6).

The increased flexibility of the PLLA–ESO copolymer was accompanied with an increase in tensile strength, yield stress, and modulus. The yield stress, for example, increased from 33.7 MPa for the linear PLLA to 35.6 MPa for PLLA–ESO(700/4), the elongation-at-break of linear PLLA is less than that of PLLA–ESO(700/4) copolymer. Results on these tensile properties suggest that PLLA–ESO(700/4) has better ductility than linear PLLA, which should be ascribed to long chain segment of $-CH_2-$ of ESO.

## Conclusions

Star-shaped PLLA–ESO copolymers could be synthesized by the bulk copolymerization of L-LA and ESO with stannous octanoate as the catalyst. The weight average molecular weight of PLLA–ESO copolymers could be controlled by variation of molar ratios of L-LA to ESO, while the amount of catalyst almost has no influence on it. The polymerization rate becomes slow with increasing concentrations of monomer to catalyst, while the molecular weight distribution decreases. Thermal analysis indicates that the PLLA–ESO copolymers possess lower glass transition temperature, melting point, crystallinity, and maximum decomposition temperature than those of neat polylactide, moreover, the oxidation resistance of PLLA–ESO copolymers has been improved compared to that of linear PLLA. Tensile testing demonstrates that PLLA–ESO copolymer exhibits improved elongation-at-break along with a plastic deformation.

**Acknowledgements** The work was financially supported by Natural science fund for colleges and universities in Jiangsu Province (Project No. 08KJB430004), Scientific and Technological Developing Scheme of of Zhenjiang City (Project No. SH2008073).

## References

1. Vink ETH, Rabago KR, Glassner DA, Gruber PR (2003) Applications of life cycle assessment to NatureWorks$^{TM}$ polylactide (PLA) production. Polym Degrad Stab 80:403–419
2. Kale G, Auras R, Singh SP, Narayan R (2007) Biodegradability of polylactide bottles in real and simulated composting conditions. Polymer Test 26(8):1049–1061
3. Garlotta D (2002) A literature review of poly(lactic acid). J Polym Environ 9(2):63–84
4. Li YJ, Shimizu H (2007) Toughening of polylactide by melt blending with a biodegradable poly(ether)urethane elastomer. Macromol Biosci 7(7):921–928
5. Signori F, Coltelli MB, Bronco S (2009) Thermal degradation of poly (lactic acid) (PLA) and poly (buty-lene adipate-co-terephthalate) (PBAT) and their blends upon melt processing. Polym Degrad Stab 94(1):74–82
6. Anderson KS, Lim SH, Hillmyer MA (2003) Toughening of polylactide by melt blending with linear low-density polyethylene. J Appl Polym Sci 89(14):3757–3768

7. Lu JM, Qiu ZB, Yang WT (2007) Fully biodegradable blends of poly(L-lactide) and poly(ethylene succinate): miscibility, crystallization, and mechanical properties. Polymer 48(14):4196–4204
8. Baek KY, Kamigaito M, Sawamoto M (2001) Star-shaped polymers by metal-catalyzed living radical polymerization1. Design of Ru(II)-based systems and divinyl linking agents. Macromolecules 34:215–221
9. Gong FR, Cheng XY, Wang SF, Wang Y, Yun Gao, Cheng SJ (2009) Biodegradable comb-dendritic tri-block copolymers consisting of poly (ethylene glycol) and poly (L-lactide): synthesis, characterizations, and regulation of surface morphology and cell responses. Polymer 50(13):2775–2785
10. Yuan WZ, Zhu L, Huang XB, Zheng SX, Tang XZ (2005) Synthesis, characterization and degradation of hexa-armed star-shaped poly(L-lactide)s and poly(D, L-lactide)s initiated with hydroxyl-terminated cyclotriphosphazene. Polym Degrad Stab 87(3):503–509
11. Danko M, Libiszowski J, Wolszczak M, Racko D, Duda A (2009) Fluorescence study of the dynamics of a star-shaped poly(-caprolactone)s in THF: a comparison with a star-shaped poly(L-lactide)s. Polymer 50(10):2209–2219
12. Castillo RV, Müller AJ (2009) Crystallization and morphology of biodegradable or biostable single and double crystalline block copolymers. Prog Polym Sci 34(6):516–560
13. Dong CM, Qiu KY, Gu ZW, Feng XD (2001) Synthesis of star-shaped poly(ε-caprolactone)-b-poly-(D, L-lactic acid-alt-glycolic acid) with multifunctional initiator and stannous octanoate catalyst. Macromolecules 34:4691–4696
14. Choi YK, Bae YH, Kim SW (1998) Star-shaped poly(ether-ester) block copolymers: Synthesis, characterization and their physical properties. Macromolecules 31:8766–8774
15. Tomalia DA, Dvornic PR (1994) What promise for dendrimers? Nature 372:617–618
16. Fre'chet JM (1994) Functional polymers and dendrimers: reactivity, molecular architecture, and interfacial energy. Science 263(5154):1710–1715
17. Trollsas M, Hedrick JL (1998) Dendrimers-like star polymers. J Am Chem Soc 120:4644–4651
18. McKee MG, Unal S, Wilkes GL, Long TE (2005) Branched polyesters: recent advances in synthesis and performance. Prog Polym Sci 30(5):507–539
19. Heise A, Diamanti S, Hedrick JL, Frank CW, Miller RD (2001) Investigation of the initiation behavior of a dendritic 12-arm initiator in atom transfer radical polymerization. Macromolecules 34:3798–3801
20. Arvanitoyannis I, Nakayama A, Kawasaki N, Yamamoto N (1995) Novel star-shaped polylactide with glycerol using stannous octoate or tetraphenyl tin as catalyst: 1. Synthesis, characterization and study of their biodegradability. Polymer 36(15):2947–2956
21. Han DK, Hubbell JA (1996) Lactide-based poly(ethylene glycol) polymer networks for scaffolds in tissue engineering. Macromolecules 29:5233–5235
22. Dong CM, Qiu KY, Gu ZW, Feng XD (2001) Synthesis of star-shaped poly(D, L-lactic acid-alt-glycolic acid) with multifunctional initiator and $SnOct_2$ catalyst. Polymer 42:6891–6896
23. Arvanitoyannis I, Nakayama A, Psomiadou E, Kawasaki N, Yamamoto N (1996) Synthesis and degradability of a novel aliphatic polyester based on L-lactide and sorbitol: 3. Polymer 37(4):651–660
24. Arvanitoyannis I, Nakayama A, Kawasaki N, Yamamoto N (1995) Novel polylactides with aminopropanediol or aminohydroxymethylpropanediol using stannous octoate as catalyst; synthesis, characterization and study of their biodegradability: 2. Polymer 36(11):2271–2279
25. Fathilah A, Chang YW, Kang SC, Yoon JY (2009) Thermal, mechanical and rheological properties of poly(lactic acid)/epoxidized soybean oil blends. Polym Bull 62:91–98
26. Choi JS, Park WH (2003) Thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate plasticized by biodegradable soybean oil. Macromol Symp 197:65–76
27. Hyon SH, Jamshidi K, Ikada Y (1997) Synthesis of polylactides with different molecular weights. Biomaterials 18:1503–1508
28. Fischer EW, Sterzel HJ, Wegner G (1973) Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. Colloid Polym Sci 251(11):980–990
29. Sosnowski S (2001) Poly(L-lactide) microspheres with controlled crystallinity. Polymer 42(2): 637–643
30. Jamshidi K, Hyon SH, Ikada Y (1988) Thermal characterization of polylactides. Polymer 29(12):2229–2234