Polym. Bull. (2011) 66:187–197
DOI 10.1007/s00289-010-0268-z

ORIGINAL PAPER

Synthesis of poly(ethylene adipate-*co*-L-lactic acid) copolymers via ring opening polymerization

Ji Liu · Peng Chen · Jun Li · Sheng-H Jiang · Zhi-Q Jiang · Qun Gu

Received: 5 January 2010 / Revised: 1 March 2010 / Accepted: 7 March 2010 /

Abstract Poly(ethylene adipate-*co*-L-lactic acid) (PLEA) copolymers were prepared via ring opening polymerization from L-lactide and hydroxyl terminated poly(ethylene adipate) prepolymer as starting materials. The composition and microstructure of the PLEA copolymers were characterized by nuclear magnetic resonance (^{1}H NMR) spectra. Results confirmed the incorporation of lactic acid segments into the chain of PLEA copolymers as well as the existence of ester exchange reaction. The thermal behaviors and thermal stability of the resultant PLEA copolymers were evaluated by differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA), respectively; and the crystal structure was confirmed by using wide-angle X-ray diffraction (WAXD). Results showed that those properties of the PLEA copolymers showed high dependence on the composition of the copolymers.

Keywords Ethylene adipate · L-Lactic acid · Ring opening polymerization

Introduction

Biodegradable polymers have been investigated for many years for their excellent performances in the pharmaceutical and biomedical applications. Among the biodegradable polymers, poly (lactic acid) (PLA), which can be derived from renewable resources, has attracted growing interests as one of the most promising and competive biodegradable materials, for its perfect combination of excellent biocompatibility and biodegradability as well as mechanical properties [1–3]. Generally, the synthesis routines of PLA could be directly divided into polycondensation reaction

---

J. Liu · P. Chen · J. Li · S.-H. Jiang · Z.-Q. Jiang · Q. Gu (✉)
Ningbo City Key Laboratory of Polymer Materials, Ningbo Institute of Material Technology and Engineering Chinese Academy of Sciences, Ningbo 315201, Zhejiang, People's Republic of China
e-mail: guqun@nimte.ac.cn

from lactic acid and ring opening polymerization (ROP) from lactides. Commonly, the former method may produce PLA products with relatively lower molecular weights compared with the that made from the latter one, and the latter has currently been serving as a more efficient approach to synthesize high-molecular-weight PLA regulated by several organometallic catalysts; furthermore, a coordination-insertion mechanism has been proposed and widely accepted [3–10]. However, despite of the growing interests for its biomedical and pharmaceutical applications, many properties of PLA products still fall short of those required for some potential applications, due to its lackage of toughness and impact resistance [4, 11, 12].

Aliphatic polyesters, such as poly(ethylene adipate) (PEA), exhibits excellent flexibility, whereas its mechanical strength is relatively poor and cannot meet various requirements due to its relatively low melting temperature (ca. 60 °C) [13–15]. Furthermore, as one of the most common aliphatic polyesters prepared from diacids and diols, PEA is also expected to be an economically competitive biodegradable polymer for its potent to be degraded and assimilated completely by microorganisms, as well as its low cost [16–18].

Structural changes or composition modifications have been regarded as effective approaches to improve the properties of the polymers and promote its application to a much broader range [11, 19, 20]. Taking into consideration the difference in chain flexibility and physical properties between PLA and PEA, it seems of interest to prepare poly(ethylene adipate-*co*-lactic acid) copolymer with hard PLLA and soft PEA segments sharing the merits of PLA such as biocompatibility and biodegradability and PEA such as flexibility and thermal properties. Up to now, few related works have been reported on such a copolymer.

In this article, we describe the synthesis of poly(ethylene adipate-*co*-L-lactic acid) (PLEA) copolymers with various compositions form hydroxyl terminated PEA prepolymers and L-lactide via bulk ROP with stannous octoate ($SnOct_2$) as catalyst. ^1H NMR, DSC, TGA, and wide-angle X-ray diffraction (WAXD) were utilized to investigate the chemical structure and properties of the resultant PLEA copolymers. Moreover, taking into the consideration of excellent biodegradable performance of PLLA and PEA, the PLEA copolymers are expected to be good alternatives for the non-degradable polymers in various applications.

Experimental

Materials

Adipic acid (AA) (CR grade), ethylene glycol (EG) (CR grade) were purchased from Yangzi Petrochemical Co. Ltd., stannous octoate (AR grade), zinc oxide (AR grade), and stannous chloride (AR grade) were provided from Sinopharm Chemical Reagent Co. Ltd, L-lactic acid (LA) (CR grade) was purchased from PURAC.

Synthesis of L-lactide

L-Lactide was synthesized from LA according to the method described in the literature [9]. 100 mL of LA was fed into a 250 mL three-neck flask, and water was distilled at 90 °C for 1 h under vacuum at 600 mmHg. Polycondensation reaction was carried out at 140 °C for 3 h in the presence of 2 wt% zinc oxide at 100 mmHg. L-Lactide was distilled from the flask at 2 mmHg at about 200 ∼ 210 °C. The resultant L-lactide was purified by recrystallization for three times from dry ethyl acetate, and then vacuum-dried at 50 °C for 24 h.

Synthesis of hydroxyl terminated poly(ethylene adipate) prepolymer

Poly(ethylene adipate) prepolymer was synthesized by a two-stage preparation procedure, including esterification and polycondensation, in a 1 L polymerizing reactor. AA and EG with a feeding molar ratio 1/2 were added into the reactor, with 0.1 wt% stannous chlorides as catalyst. The reactor was evacuated and then filled with nitrogen for several times, in order to remove all of the oxygen. Then, the mixture was heated to 200 °C under stirring of 60 rpm with reaction pressure of 0.35 MPa for 4 h to eliminate the water generated. The esterification procedure was considered complete after the collection of a theoretical amount of H_2O, which was removed from the reaction mixture by distillation and collected in a graduate cylinder.

A vacuum system was applied slowly for 30 min till the vacuum was controlled under 100 Pa, to avoid excessive foaming and minimize prepolymer sublimation, which is a potential problem during the polycondensation procedure. The polycondensation continued for 1 h, and the PEA prepolymer was removed, cooled, and milled. The PEA prepolymer was dissolved in chloroform and precipitated with methanol, then filtered and dried under vacuum at 40 °C to a constant weight for use.

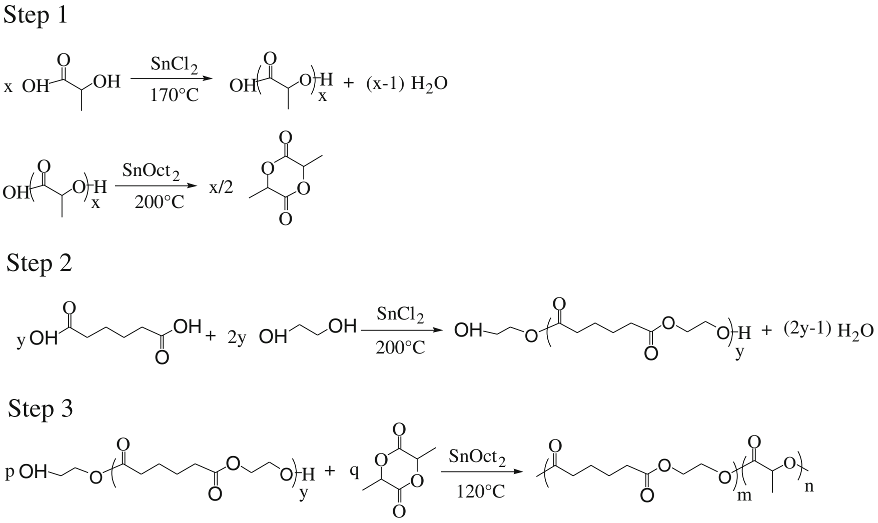
Synthesis of PLEA copolymers via ring opening polymerization

Different molar ratio of hydroxyl terminated PEA prepolymer and L-lactide mixed with stannous octoate (1 wt% with respect to the reactants) were added into a one-neck flask; after degassing, the flask was sealed under vacuum and the polymerization was proceeded at 120 °C for 24 h. The resultant copolymers were dissolved in chloroform initially and then precipitated by adding excessive amount of cold methanol under stirring. Finally, the precipitants were filtered and washed by methanol, then dried under vacuum at 40 °C up to constant weight. The synthesis routine was shown in Scheme 1.

Analytical procedures

Gel permeation chromatography (GPC) characterization

The number-average molecular weights (M_n), weight-average molecular weights (M_w), and polymerization dispersion index (PDI) of the PLEA copolymers were measured by a Waters-2414 GPC equipped with a refractive index detector and PL Gel 5 μm mixed-D type column. Chloroform was used as mobile phase at a flow rate of 1 mL/min and polystyrene solution was used as the calibration standard. Two



Scheme 1 Synthesis routine of PLEA copolymers via ring opening polymerization

hundred milliliters of 0.5 wt% polymer solution in chloroform was injected into the run. M_n, M_w, and PDI were calculated with the Maxima 820 software.

NMR characterization

Purified copolymer of 10 ~ 20 mg was dissolved into 0.5 mL chloroform-*d*. ^{1}H-NMR was recorded on a Brucker-spectrometer at 25 °C with a resonance frequency of 400 MHz.

Thermal analysis

The melting and crystallization parameters were measured by a METTLER TOLEDO-DSC I equipped with a refrigerated cooling system. A sample of 5 ~ 10 mg sealed in an aluminum pan was first heated to 180 °C at 40 °C/min with a nitrogen flow of 50 mL/min, held for 3 min to remove the thermal history, and then cooled to −50 °C at 10 °C/min, finally heated again to 180 °C at 10 °C/min. Thermal degradation behaviors and thermal stability were carried out by using METTLER TOLEDO-TGA/DSC I, and TGA diagrams were recorded from 25 to 800 °C at 10 °C/min with a nitrogen flow of 50 mL/min.

Wide-angle X-ray diffraction (WAXD)

Wide-angle X-ray diffraction patterns were recorded at room temperature by using a Bruker D8 diffractometer at 40 kV and 30 mA. All the samples were molded into films of 1 ± 0.2 mm thick and isothermally crystallized at their respective crystallization temperature (decided by DSC) for 4 h before use.

Results and discussion

Chemical structure and compositions

Commonly, low molecular weight is an inherent characteristic for aliphatic polyesters prepared by polycondensation reaction due to the presence of competitive reaction between polycondensation and thermal degradation, which will concurrently occur [12]. Hydroxyl terminated PEA prepolymer with lower molecular weight could be easily gained by melting polycondensation reaction with excessive molar feeding of EG. Figure 1a illustrates the ^{1}H NMR spectra of hydroxyl terminated PEA prepolymer synthesized via polycondensation reaction for 1 h. The proton resonance signals arise at $\delta = 1.67$ (s, ^{2}H), 2.36 (s, ^{1}H), 3.74 (s, ^{6}H), 3.82 (m, ^{4}H), 4.22 (m, ^{5}H), and 4.27 ppm (s, ^{3}H), and the assignment of the signals is shown in accordance with the digital numbers marked in the structural formula of the hydroxyl terminated PEA prepolymer. Among the proton signals, $\delta = 3.74$ (s, ^{6}H), 3.82 (m, ^{4}H), 4.22 ppm (m, ^{5}H) were reasonably attributed to those protons in the end groups. Whereas the carboxylic end group could not be distinctly resolved for the overdosed feeding of EG and the limit of instrumental resolution, as well as the week discrepancy between the effect of carboxylic group and ester group on the intermediate methylene.

The relative integrity value of the methylene proton signals could be used to calculate the degree of polymerization (D_p) and number-average molecular weight ($M_\mathrm{n,\ NMR}$) of hydroxyl terminated PEA prepolymer by using Eq. 1 [11]:

$$\begin{aligned} D_\mathrm{p} &= \frac{I_1}{I_4} + 1, \\ M_\mathrm{n,NMR} &= 172 \times D_\mathrm{P} + 2, \end{aligned} \tag{1}$$

where I_1 and I_4 represent the intensity of methylene peak of EG located in the internal and end of PEA prepolymer's molecular chain, 172 and 2 the masses of repeating unit of EA segments and hydrogen atoms at the end of PEA prepolymer's molecular chain, respectively. The value of $M_\mathrm{n,\ NMR}$ of PEA was 7876 g/mol, corresponding closely to $M_\mathrm{n,\ GPC}$ 8,100 g/mol, which was gained from GPC measurement and listed in Table 1.

Figure 1b illustrated the ^{1}H NMR spectra of L-lactide and merely two distinct proton resonance signals emerging at $\delta = 1.68$ (d, ^{7}H) and 5.04 ppm (m, ^{6}H) could be detected, and the assignment of these two signals were shown in the structural formula of L-lactide. No finding of other signals from the impurities also confirms the high purity of the L-lactide product as well as the high efficiency of re-crystallization process.

Typical ^{1}H NMR spectrum of resultant PLEA copolymers was illustrated in Fig. 1c. It was found that all the intrinsic proton resonance signals for PEA and PLLA homopolymers were all detected at chemical shifts of $\delta = 2.38$ (s, ^{1}H), 1.69 (s, ^{2}H), 4.28 ppm (m, ^{3}H) for PEA, as well as 5.09 (m, ^{4}H) and 1.51 ppm (m, ^{5}H) for PLLA, respectively. Moreover, other new signals were also found at chemical shifts at $\delta = 1.58$ (m, ^{6}H), 5.19 (m, ^{7}H), 4.37 (s, ^{8}H), and 2.43 ppm (s, ^{9}H), the

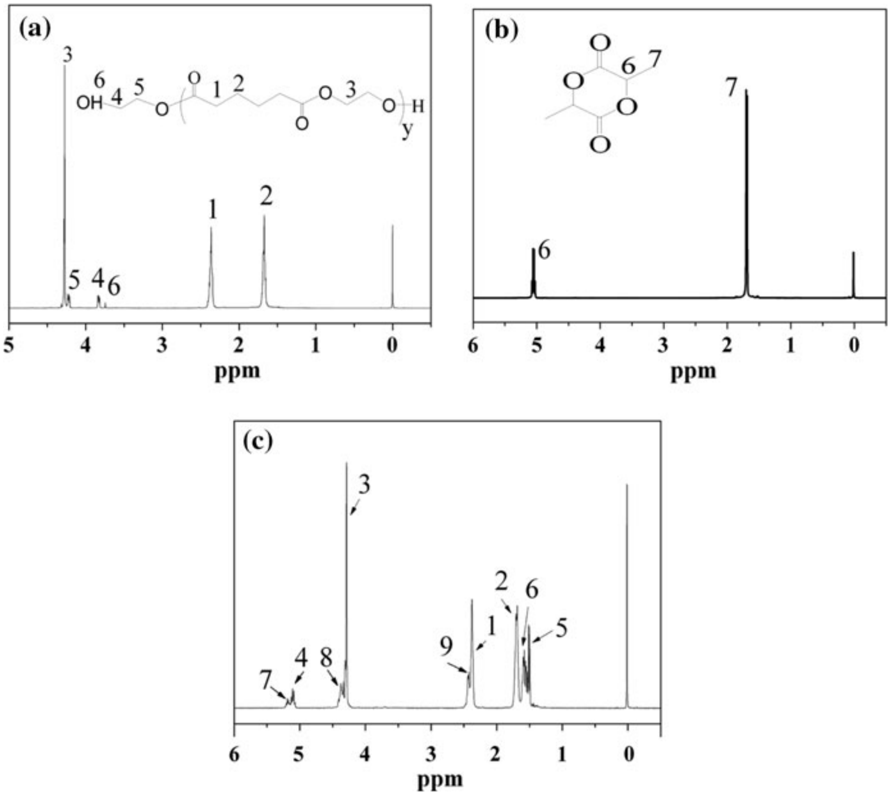
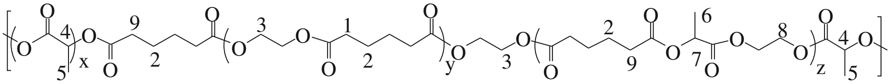


Fig. 1 ^{1}H NMR spectra of PEA prepolymer (**a**), L-lactide (**b**), and PLEA copolymers (**c**)

Table 1 Composition and molecular weights of PLLA, PEA, and PLEA copolymers

Samples	Feeding ratio		Composition		f_{LA} (%)	$M_{n,\ GPC}$ (g/mol)	$M_{w,\ GPC}$ (g/mol)	PDI
	EA	LA	EA	LA				
PEA	1	0	1	0	0	8100	14,800	1.83
PLEA-1	1	2	1	1.72	63.2	13,300	21,200	1.59
PLEA-2	1	3	1	2.90	74.4	16,600	24,500	1.48
PLEA-3	1	9	1	8.21	89.1	17,800	27,600	1.55
PLLA	0	1	0	1	100	20,400	34,100	1.67

assignment of which was marked in the sequence structure of PLEA copolymer in Scheme 2. The formation of ester bond between LA and AA, as well as LA and EG indicated the incorporation of LA segments in the resultant copolymers. Furthermore, it also confirmed the occurrence of ester exchange reaction between the LA and EA segments; otherwise, no other new signals could be detected aside from the intrinsic resonance signals for EA and LA segments [12, 21, 22].



Scheme 2 Assignment of protons in PLEA copolymers

The mass ratio of different segments and content of LA segments in the PLEA copolymers could also be deducted from the relative integrity values of the proton signals in EA and LA segments (Eq. 2):

$$\begin{aligned}\frac{m_{\mathrm{EA}}}{m_{\mathrm{LA}}} &= \frac{(I_1 + I_9) \times 172 \times 3}{(I_5 + I_6) \times 72 \times 4},\\ f_{\mathrm{LA}} &= \frac{m_{\mathrm{LA}}}{m_{\mathrm{LA}} + m_{\mathrm{EA}}} \times 100\%,\end{aligned} \tag{2}$$

where $m_{\mathrm{EA}}/m_{\mathrm{LA}}$ represents the mass ratio of EA to LA segments, f_{LA} the content of LA segments in the PLEA copolymers, $(I_1 + I_9)$ and $(I_5 + I_6)$ the relative integrity value of methylene proton resonance peaks for EA and LA segments, 172 and 72 the masses of EA and LA repeating units, digital number 3 and 4 the number of protons in the methylene groups for LA and EA segments, respectively.

The value of f_{LA} and $m_{\mathrm{EA}}/m_{\mathrm{LA}}$ were also listed in Table 1. It is obvious that the conversions of L-lactide (or lactic acid) for all the PLEA copolymers are all lower than 1. This phenomenon may be attributed to either the partial sublimation of the L-lactide monomer during the process of polymerization or the reversibility of the ROP, which results in a certain content of the residual monomers at equilibrium and ultimately dispelled during the process of purification [12, 22], or both the two.

Molecular weights $M_{\mathrm{n,\ GPC}}$ and $M_{\mathrm{w,\ GPC}}$ as well as PDI of PLLA, PEA, and PLEA copolymers measured from GPC were also listed in Table 1. Moreover, it is found that increase in LA feeding ratio is in favor of increasing the molecular weights of PLEA copolymers. Furthermore, PDI of PLEA copolymers and PLLA homopolymer are all ranging from 1.4 to 1.7, suggesting a relative low weight molecular weight dispersion.

Thermal properties of PLEA copolymers

As known to us, since the copolymerization reaction alters the composition as well as the regularity of the polymer chains, the thermal behaviors are thus changed. The content of the segments is always considered to be a key ingredient, which decides the properties of the resultant copolymers. Therefore, it is of importance to investigate the dependence of thermal properties on the content of the segments [10, 21]. DSC analysis of the PLEA copolymers with different compositions was carried out and the DSC curves of PLEA copolymers were showed in Fig. 2a, b. All the PLEA copolymers exhibited crystalline behaviors similar to that of PLLA or PEA homopolymer and only one distinct crystallization and melting peak can be detected for PLEA copolymers, irrespective of the content of LA segments. It is obvious that T_{m} (Fig. 2b) and T_{c} (Fig. 2a) of PLLA homopolymer are much higher than that of PEA homopolymer, while T_{m} and T_{c} of PLEA copolymers are all intermediate

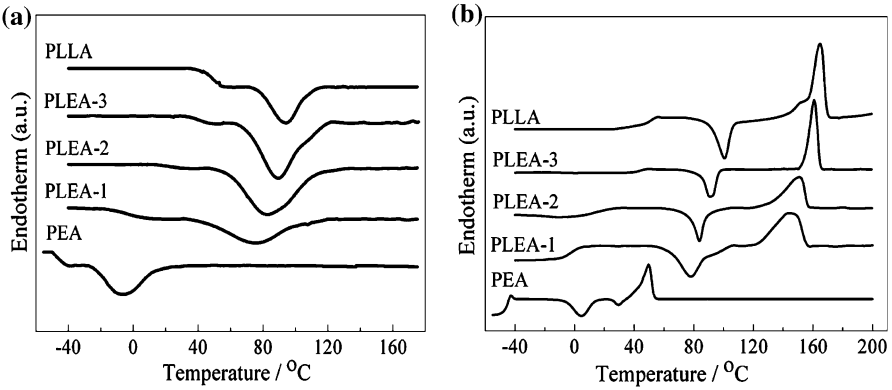


Fig. 2 DSC cooling scans (**a**) and heating scans (**b**) of PLLA, PEA, and PLEA copolymers

between the two. It suggests that the crystallization and melting behavior of PLEA copolymers were dominated by LA segments, while EA segments remained amorphous in the PLEA copolymers. When the content of LA segments increased, it became easier for the LA segments to fold while regularity of EA segments dropped down dramatically via ester exchange reaction, leading to the disappearance of melting and crystallization peaks intrinsic for PEA homopolymer. However, to validate this hypothesis, more evidence should be provided, such as WAXD patterns, which are to be discussed latter.

As shown it Fig. 2, it could be found that T_g, T_m, and T_c observed gradually increases with more LA segments incorporated into the polymer chains, from PLEA-1 to PLEA-3. This tendency is attributed to the inferior flexibility of LA segments compared with EA segments, which could be drawn by the evidence that T_g of PLLA homopolymer (ca. 47 °C) is much higher than that of PEA homopolymer (ca. −46 °C). The increase in T_m and T_c of the PLEA copolymers with higher LA content (or lower EA content) could attribute to the two possible functions of EA segments; the first one is that EA segments serve as soft blocks to increase the chain flexibility of PLEA copolymers, and the other one is acting as heterogeneous blocks to decrease the chain regularity of PLEA copolymers. That is why the decrease in EA content results in increasing crystallization ability of the LA segments, which further contributes to the increase of T_m.

Thermal stability of PEAL copolymers

The thermal degradation analysis and thermal stability of the PLEA copolymers were evaluated by using TGA. PLLA is widely acknowledged to be a relatively thermally unstable material and the decomposition temperature of the ester bond also exhibited extremely high dependence on the chemistry structure of PLLA copolymers [2, 3]. Thus, studies of PLLA copolymers were always focused on increasing the thermal stability of the copolymers. Figure 3a presents the thermal degradation behavior of the PLEA copolymers with different compositions. All the PLEA copolymers exhibited the same tendency of weight loss curves with two distinct decomposition steps. In the DTG curves (not presented here), two obvious peaks were detected at ca. 250 and 310 °C, which were corresponding with the intrinsic maximum decomposition temperature for PLLA and PEA homopolymers, respectively, irrespective of the content of LA segments, while only one can be detected for PLLA and PEA homopolymers. The dependence of the first maximum thermal degradation temperature $T_{\max1}$ (corresponding to LA segments) and the second maximum thermal degradation temperature $T_{\max2}$ (corresponding to EA segments) on the content of LA segments was illustrated in Fig. 3b. It is obvious that $T_{\max1}$ and $T_{\max2}$ increase with decreasing LA segments (or increasing EA segments) incorporated into the PLEA copolymers, attributing to the relative higher maximum thermal degradation temperature for EA segments compared with LA segments.

Thermal parameter of the onset temperature for thermal degradation $T_{5\%}$ (5% weight loss) was used to evaluate the thermal stability of the PLEA copolymers, and the higher the value is the more stable it is for the samples opened to heat, vice versa. The effect of LA content on $T_{5\%}$ was also demonstrated in Fig. 3b, and it can be found that $T_{5\%}$ of the PLEA copolymers were drastically depended on the composition of the resultant copolymer, and it increased with decreasing LA content (or increasing EA content). In other words, the thermal stability could be efficiently improved by increasing the amount of EA content in the PLEA copolymers.

Crystalline morphology

The WAXD patterns of PLLA, PEA homopolymers, and PLEA copolymers are shown in Fig. 4. The diffractions peaks of PLLA at $2\theta = 14.77°$, 16.71°, 19.09°, 22.42° are in accordance with the crystal planes of (010), (110), and (200), (111) and (201), (102), and (210) [23], respectively. The diffractions peaks for PEA at $2\theta = 20.56°$, 21.81°, 24.66° are detected, which are assignable to be the crystal planes of $(11\bar{1})$, (110), and (020) [18, 24], respectively.

For PLEA copolymers synthesized with different feeding ratios, the diffraction peaks appear at 14.77°, 16.71°, 19.09°, and 22.42°, which are observed for PLLA

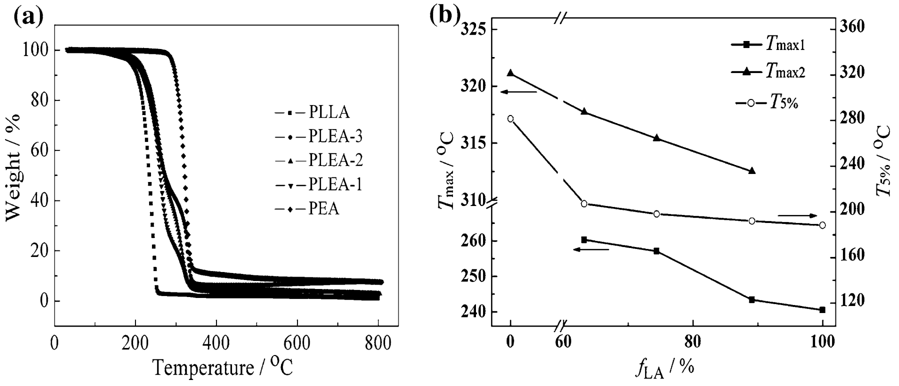
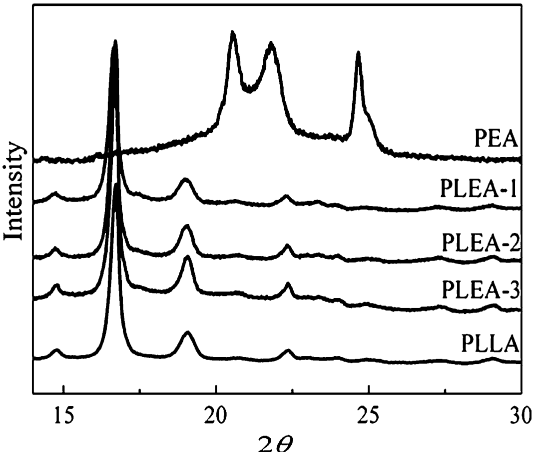


Fig. 3 TGA traces of PLLA, PEA, and PLEA copolymers (**a**) and effect of f_{LA} on thermal properties (**b**)

Fig. 4 WAXD patterns of PLLA, PEA, and PLEA copolymers



homopolymer. Moreover, almost all the intrinsic diffraction peaks of PEA, especially the ultra strong diffraction peaks at 20.56° and 24.66° disappeared for PLEA copolymers, irrespective of the content of EA segments in the resultant PLEA copolymers. This may be in accord with the phenomena observed in the section of DSC, in which no intrinsic melting or cooling peaks for PEA homopolymer could be detected. Furthermore, it further confirms that only LA segments retain their crystal structures in the PLEA copolymers while EA segments remain amorphous, attributing to the irregularity of EA segments caused by the ester exchange reaction during the ROP.

Conclusions

A series of PLEA copolymers with various compositions was synthesized from hydroxyl terminated PEA prepolymer and L-lactide with stannous octoate ($SnOct_2$) as catalyst via ROP. ^1H NMR characterizations confirmed the incorporation of LA and EA segments, and increase of the LA content with more L-lactide fed in the PLEA copolymers. GPC data showed that molecular weights increased with higher feeding ratio of L-lactide. DSC analysis and WAXD patterns demonstrated that the crystal structures in PLEA copolymers were dominated by LA segments, while EA segments remained amorphous due to the existence of ester exchange reaction during the polymerization process. Moreover, T_m, T_c, and T_g increased with less EA segments incorporated into the PLEA copolymers. Thermal stability and thermal degradation behaviors were evaluated by TGA measurement and results illustrated that incorporation of EA segments was in favor of increasing the thermal stability of PLEA copolymers, and T_{max1}, T_{max2}, and $T_{5\%}$ increased with more EA segments incorporated in the PLEA copolymers.

Acknowledgments This works was financially supported by the Key Projects in the National Science & Technology Pillar Programs (Contract No. 2007BAE28B06), and Zhejiang Provincial Major Science & Technology Special Projects (Contract No. 2008C11092-2).

References

1. Okada M (2002) Chemical syntheses of biodegradable polymers. Prog Polym Sci 27(1):87–133
2. Gupta B, Revagade N, Hilborn J (2007) Poly (lactic acid) fiber: an overview. Prog Polym Sci 32(4):455–482
3. Garlotta D (2001) A literature review of poly (lactic acid). J Polym Environ 9(2):63–84
4. Mehta R, Kumar V, Bhunia H, Upadhyay SN (2005) Synthesis of poly (lactic acid): a review. J Macromol Sci Polym Rev C45(4):325–349
5. Albertsson AC, Srivastava RK (2008) Recent developments in enzyme-catalyzed ring-opening polymerization. Adv Drug Deliver Rev 60(9):1077–1093
6. Thomas CM (2010) Stereocontrolled ring-opening polymerization of cyclic esters: synthesis of new polyester microstructures. Chem Soc Rev 39(1):165–173
7. Albertsson AC, Varma IK (2003) Recent developments in ring opening polymerization of lactones for biomedical applications. Biomacromolecules 4(6):1466–1486
8. Yu CP, Zhang LF, Tu KH, Shen ZQ (2004) Ring-opening polymerization of (D, L)-lactide by the single component rare earth tris (4-tert-butylphenolate)s. Polym Bull 52(5):329–337
9. Kulkarni RK, Moore EG, Hegyeli AF, Leonard F (1971) Biodegradable poly (lactic acid) polymers. J Biomed Mater Res 5(3):169–181
10. Li B, Chen SC, Qiu ZC et al (2008) Synthesis of poly(lactic acid-b-p-dioxanone) block copolymers from ring opening polymerization of p-dioxanone by poly(L-lactic acid) macroinitiators. Polym Bull 61(2):139–146
11. Zeng JB, Li YD, Zhu QY et al (2009) A novel biodegradable multiblock poly (ester urethane) containing poly (L-lactic acid) and poly (butylene succinate) blocks. Polymer 50(5):1178–1186
12. Ba CY, Yang J, Hao QH et al (2003) Syntheses and physical characterization of new aliphatic triblock poly (L-lactide-b-butylene succinate-b-L-lactide)s bearing soft and hard biodegradable building blocks. Biomacromolecules 4(6):1827–1834
13. Kim SW, Lim JC, Kim DJ, Seo KH (2004) Synthesis and characteristics of biodegradable copolyesters from the transesterification of poly (butylene adipate-co-succinate) and poly (ethylene terephthalate). J Appl Polym Sci 92(5):3266–3274
14. Siriphannon P, Monvisade P (2008) Preparation and characterization of hydroxyapatite/poly (ethylene adipate) hybrid composites. J Biomater Sci Polym Ed 19(7):925–936
15. Monvisade P, Loungvanidprapa P (2007) Synthesis of poly (ethylene adipate) and poly (ethylene adipate-co-terephthalate) via ring-opening polymerization. Eur Polym J 43:3408–3414
16. Atkins TW (1998) Biodegradation of poly (ethylene adipate) microcapsules in physiological media. Biomaterials 19(1–3):61–67
17. Jin HJ, Lee BY, Kim MN, Yoon JS (2000) Properties and biodegradation of poly (ethylene adipate) and poly(butylene succinate) containing styrene glycol units. Eur Polym J 36(12):2693–2698
18. Kim MN, Kim KH, Jin HJ et al (2001) Biodegradability of ethyl and n-octyl branched poly (ethylene adipate) and poly (butylene succinate). Eur Polym J 37(9):1843–1847
19. Kramer JW, Treitler DS, Dunn EW et al (2009) Polymerization of enantiopure monomers using syndiospecific catalysts: a new approach to sequence control in polymer synthesis. J Am Chem Soc 131(44):16042–16044
20. Pfeifer S, Lutz JF (2007) A facile procedure for controlling monomer sequence distribution in radical chain polymerizations. J Am Chem Soc 129(31):9542–9543
21. Deng LM, Wang YZ, Yang KK et al (2004) A new biodegradable copolyester poly (butylene succinate-co-ethylene succinate-co-ethylene terephthalate). Acta Mater 52(20):5871–5878
22. Li SM, Vert M (2003) Synthesis, characterization, and stereocomplex-induced gelation of block copolymers prepared by ring-opening polymerization of L (D)-lactide in the presence of poly (ethylene glycol). Macromolecules 36(21):8008–8014
23. Yasuniwa M, Tsubakihara S et al (2006) Crystallization behavior of poly (L-lactic acid). Polymer 47(21):7554–7563
24. Nakafuku C (1998) Melting and crystallization of poly (ethylene adipate) under high pressure. Polym J 30(9):761–763