Synthesis, Characterization, and Properties of a Linear Poly(ester-amide) Containing Ethylene Glycol Lactate Sequences

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ABSTRACT: A novel linear lactic acid-based poly(ester-amide) (LLPEA) was prepared via polyaddition of toluene-2,4-diisocyanate (TDI) with ethylene lactate succinic half-ester diacid (ELDA), which contained ethylene glycol lactate sequences and derived from lactic acid. LLPEA was characterized with FTIR, GPC, DSC, TGA, and XRD. The weight average molecular weight and its polydisperse index of LLPEA could be 1.0×10^5 and 2.0, respectively. DSC and XRD analysis showed that LLPEA was a semicrystalline polymer. The glass transition temperature, melting temperature, and the thermal decomposition temperature (50 wt %) of LLPEA were −2, 94, and ~415°C, respectively. The contact angle determination indicated that LLPEA was a hydrophilic polymer. It was found that the yield strength, tensile strength, and elastic module of LLPEA could be 8.8, 9.6, and 176 MPa, respectively. In addition, the weight loss percentage of LLPEA was 2.5% after 157-days immersion in activated sludge at ambient temperature, which suggested that LLPEA was degradable. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3805–3808, 2006

Key words: linear; lactic acid-based; poly(ester-amide); synthesis; properties

INTRODUCTION

Polylactide (PLA) and its copolymers had garnered much attention for their use in biomedical and pharmaceutical applications because of their biocompatibility and biodegradability.[1–5] Thus, lactic acid moiety was commonly incorporated in polymer backbone to act as degradable points.[6]

Compared to aliphatic polyesters, aliphatic polyamides possessed higher thermal stability, higher modulus, and higher tensile strength. However, aliphatic polyamides were generally not biodegraded.[7] Combination of the characteristics of polyester and polyamide was achieved by using poly(ε-caprolactone) and PLA macromers to synthesize poly(ester-amide)s (PEAs).[8–12]

To enlarge the range of accessible properties for a wider use, PEA could be suitably tailored by varying the nature, composition, and architecture of the starting materials. Herein, a dicarboxylic-terminated oligoester that contained ethylene glycol lactate sequences was allowed to react with toluene-2,4-diisocyanate (TDI) to prepare a novel linear lactic acid-based poly(ester-amide) (LLPEA). The structure of LLPEA and its properties were investigated and presented in this article.

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EXPERIMENTAL

Materials

The dicarboxylic-terminated oligoester ELDA, with the number average molecular weight of 4019 g/mol, was prepared according to the literature[13] by using lactic acid and ethylene glycol as starting materials. Succinic anhydride, toluene-2,4-diisocyanate (TDI), methanol, chloroform, and *N*,*N*-dimethylformamide (DMF) were all analytical grade reagents (Shanghai Chemical Agents, China) and were used as received.

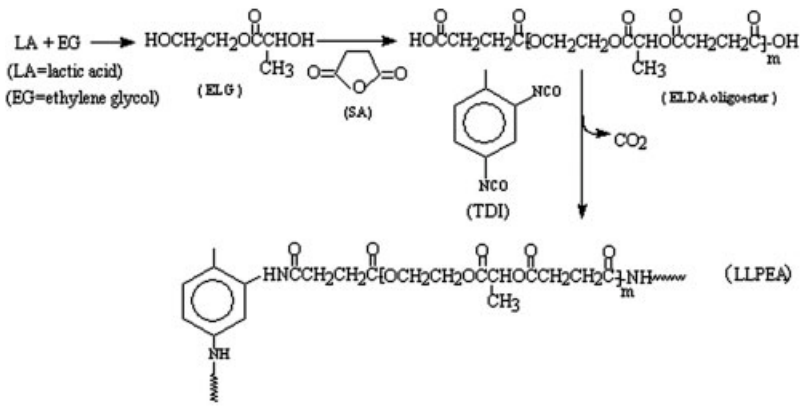
Preparation of LLPEA

LLPEA was synthesized via melt-polycondensation of TDI and ELDA. With vigorous stirring, TDI was added into 10 g melt ELDA in the molar ratio of 1.2–1.5 : 1 (TDI/ELDA). The mixture was allowed to react at 140°C for 35 min. Then, the crude polymer was dissolved in DMF and precipitated from methanol. LLPEA was dried under vacuum at ambient temperature to constant weight (9.3 g; yield, 89%).

Characterization of LLPEA

Powdered ELDA and LLPEA were mixed with dry KBr, respectively, and compressed into disk. Then, FTIR spectra of the samples were recorded using a Nexus 470 FTIR spectrometer.

X-ray diffraction profile of LLPEA was collected with a Bruker D8-Advanced diffractometer using



Scheme 1 The synthesis procedure of LLPEA.

Nickel-filtered Cu Kα radiation (λ = 0.15406 nm) and scanned from 2° to 50° at a scan speed of 2°/min.

The different scanning calorimeter (DSC) and thermogravimetric analysis (TGA) were carried out with a Universal V2.4F (TA Instruments) DSC-TGA analyzer. LLPEA was heated from −50 to 150°C at a heating rate of 10°C/min to record DSC curves and from 0 to 900°C at 20°C/min to obtain thermogravimetric profiles under nitrogen atmosphere.

The molecular weight and polydispersity index of LLPEA were measured on a PerkinElmer Series 200 gel permeation chromatography (GPC) with PL mixed column. DMF was used as eluent at a flow rate of 1.0 mL/min and polystyrene standards were employed for calibration.

Mechanical and hydrophilic properties test

LLPEA was dissolved in chloroform and cast to form films. Then the mechanical and hydrophilic properties were evaluated.

The tensile test was performed[14] at room temperature on a SANS GTM6104 Universal instrument. The tensile strength was measured at a crosshead speed of 15 mm/min and the initial distance between grips was 60 mm. The specimens were dumbbell-shaped with an overall length of 75 mm and the width of the ends was 10 mm. The length, width, and thickness of narrow parallel portion were 60, 6, and 3 mm, respectively. The data reported were averaged from five measurements.

The hydrophilic or hydrophobic property of LLPEA was examined with water contact angle, which was measured with a JC2000A digital contact angle analyzer, and an average of five measurements was taken.

In vitro degradation

The weighed 6 mm × 5 mm × 2 mm tabular samples were placed in activated sludge and maintained at ambient temperature (28 ± 5°C). At timed intervals, the samples were removed, dried under vacuum at ambient temperature, and weighed. The weight loss percentage of the samples was calculated from the initial weight of sample (W_i) and the weight of dried sample (W_d): $WL\% = (W_i - W_d)/W_i \times 100$. An average of triplicate measurements was taken.

RESULTS AND DISCUSSION

Preparation of LLPEA

LLPEA was synthesized via the polycondensation reaction between diisocyanate and dicarboxylic acid[15] (Scheme 1). To impetus the polycondensation reaction, TDI was found in excess. As it was known, TDI was very active and ready to react with the compounds or groups that contained active hydrogen. Therefore, the reaction should be carried out in anhydration condition. In addition, the reaction between —NCO group and —NH— group in the chain might result in crosslinking. To avoid forming crosslinked polymer, TDI should be homogeneously mixed with melt ELDA during the reaction procedure and end the reaction within 50 min. Then, the crude product was immediately dissolved in DMF and precipitated from methanol to deactivate the remained —NCO groups. As expected, LLPEA could be dissolved in chloroform and DMF, which indicated that it was linear. The weight average molecular weight (M_w) and its polydispersity index (PDI) of LLPEA could be 1.0×10^5 and 2.0, respectively.

Characterization of LLPEA

The structure of LLPEA, which was substantially different from that of the reagents, was verified with FTIR (Fig. 1). The FTIR spectra of LLPEA showed the characteristic absorption bands at 3439, 3366, 2969, 1734, 1601, 1530, 1387, 1217, and 1160 cm^{-1}. As shown, more characteristic absorption bands

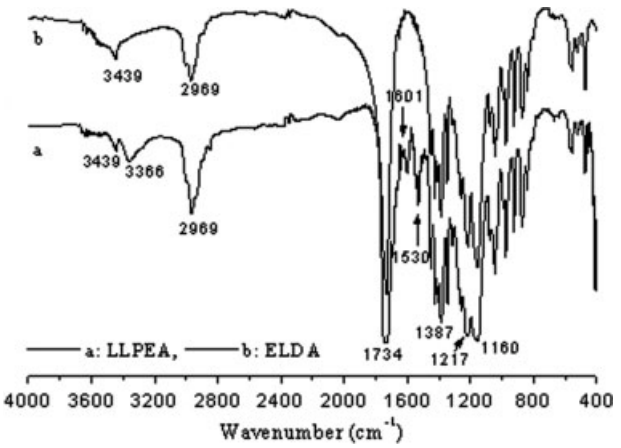


Figure 1 The FTIR spectra of the precursor ELDA and the linear lactic acid-based poly(ester amide).

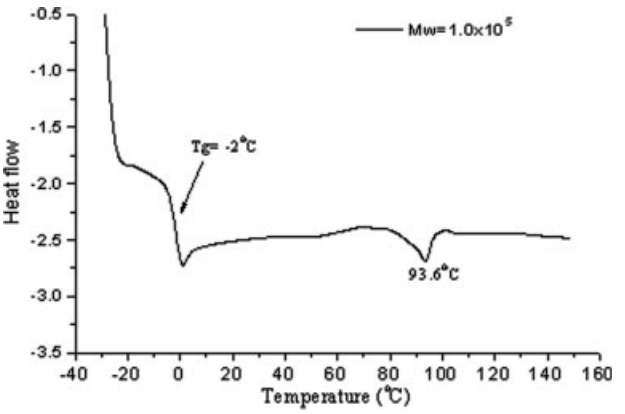


Figure 3 Differential scanning calorimetry thermogram of the linear lactic acid-based poly(ester amide).

exhibited on the FTIR spectra of LLPEA than that of ELDA. It is found that the absorption bands of benzyl and —NH— groups appeared at 1601 and 3366 cm^{-1} on the FTIR spectra of LLPEA, respectively, which suggested that the reaction between ELDA and TDI was carried out. It was also found that the characteristic peaks of amide group[16] exhibited at 1734 and 1530 cm^{-1}, which confirmed that the structure of LLPEA as well. In addition, no band was observed at 2278 cm^{-1}, indicated that no —NCO groups remained in the polymer.

There was a sharp peak exhibited at 20.4° on the XRD pattern of LLPEA (Fig. 2), which suggested that LLPEA was semicrystalline. It could be calculated that the crystallinity of the sample was approximate to 32.2%. The DSC analysis showed that the glass transition temperature (T_g) and the melt temperature (T_m) of LLPEA were −2 and ∼ 94°C, respectively (Fig. 3), which also revealed that LLPEA was semicrystalline. As the lactate groups were distributed singly along the backbone, LLPEA was more flexible than PLA and PEEA derived from PLLA and oligo(ethylene glycol). Thus, T_g of LLPEA was much lower than that of PLA (∼ 60°C)[17] and PEEA (∼ 40°C).[9]

Properties of LLPEA

There were intermolecular and intramolecular hydrogen bond interactions between or in LLPEA chains due to the amide groups. Thus, LLPEA could resist the temperature higher than 260°C. The thermal decomposition temperatures of LLPEA were 269 (1 wt % loss), 421 (50 wt % loss), and 438°C (89 wt % loss), respectively (Fig. 4).

LLPEA possessed good processing characteristics. LLPEA films could be prepared by solution casting and the films were used for mechanical, hydrophilic, and degradation tests.

As for the samples of the molecular weight in the range aforementioned, the yield strength, the tensile strength, and the elastic module were 8.0–8.8, 8.3–9.6, and 175.8–181.9 MPa, respectively (Table I). It

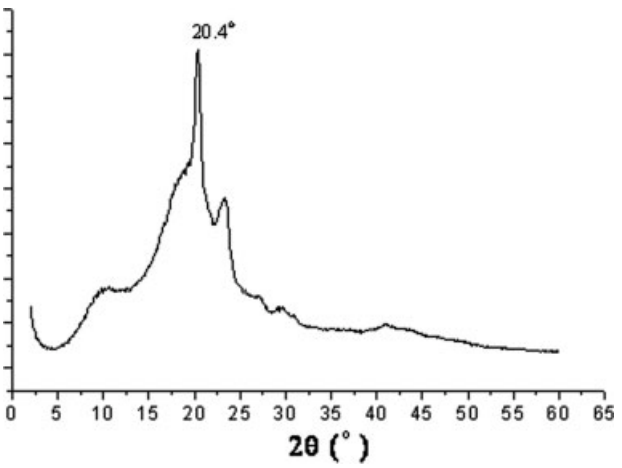


Figure 2 XRD profile of the linear lactic acid-based poly (ester amide).

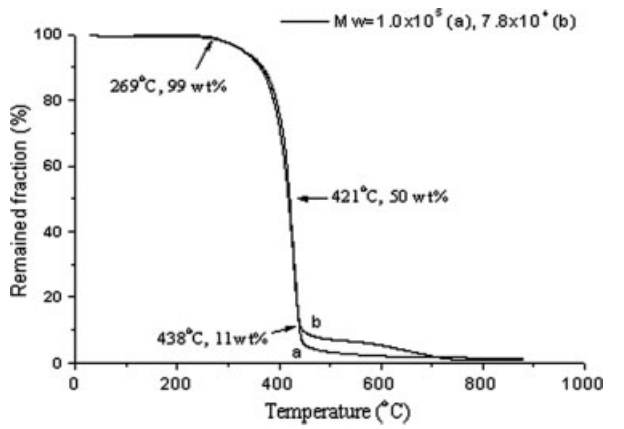


Figure 4 Thermogravimetric analysis profiles of the linear lactic acid-based poly(ester amide)s.

TABLE I
The Mechanical and Hydrophilic Properties of Linear Lactic Acid-Based Poly(ester amide)

Samples	Weight average molecular weight	Polydispersity index	Tensile strength (MPa)	Elastic module (MPa)	Yield strength (MPa)	Water contact angle (°)
LLPEA1	7.8×10^4	2.2	8.3	181.9	8.0	64
LLPEA2	1.0×10^5	2.0	9.6	175.8	8.8	52

could be anticipated that increasing its molecular weight or assuming thermal processing to prepare samples might improve the mechanical properties of LLPEA.

Owing to the hydrophilic —NH— groups, the water contact angle of LLPEA was lower than that of PLA (79° and 76° for PDLLA and PLLA, respectively).[18] The higher the molecular weight was, the more —NH— groups LLPEA contained and the lower water contact angle would be (Table I).

Attributed to the hydrolabile lactate unit incorporated, LLPEA showed degradable (Fig. 5) character. The weight loss percentage of LLPEA was 2.5% after 157-days immersion in activated sludge at ambient temperature. Thereafter, LLPEA would continue to degrade slowly.

CONCLUSIONS

A novel linear lactic acid-based poly(ester-amide) (LLPEA) was designed and synthesized. The polymer was composed of ethylene groups, amide groups, and lactate units. These structure units were singly distributed along the chain, which would keep the phase separation between the soft segments and rigid amide segments. With low T_g and solubility, LLPEA was easy to be processed. In addition, LLPEA was degradable as it contained labile lactate moiety.

It was anticipated that, by varying the chemical structure of starting materials and the length of dicarboxylic-terminated oligoester, the properties of LLPEA might be tailored to meet the requirements for biomedical or environment friendly applications.

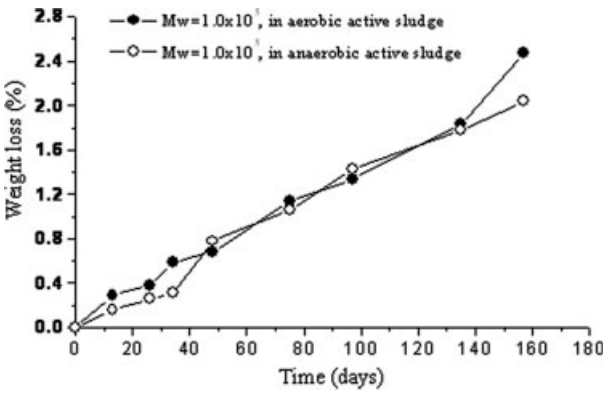


Figure 5 The *in vitro* degradation behavior of the linear lactic acid-based poly(ester amide) in activated sludge at ambient temperature.

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