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Synthesis and Characterization of a Novel Poly(ester-urethane) Containing Short Lactate Sequences and PEG moieties

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ABSTRACT: A novel poly(ester-urethane) with tailor-made structure was prepared by using lactic acid (LA) as starting material through a combination of two facile common reactions. First, a diol was prepared via the esterification between LA and poly(ethylene glycol) (PEG) with low molecular weight. Subsequently, the poly(ester-urethane) was synthesized through the addition polymerization of the LA-based diol and toluene 2,4-diisocyanate with 1,4-butanediol as chain extender. The structure, morphology, and properties of intermediate and the poly(ester-urethane) were analyzed with Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, gel permeation chromatography (GPC), X-ray diffraction, differential scanning calorimetry, polarizing optical microscopy, and thermogravimetric analysis. The results indicated that the intermediate was a diol of conjugating quite short lactate sequences with PEG oligomer, and the structure of the poly(ester-urethane) was as expected. The thermal transition, thermal decomposition temperature, and crystallinity of the polymer samples depended on the molecular size of PEG. *In vitro* degradation property of the poly(ester-urethane) also relied on the molecular weight of PEG. The weight loss percentages varied from 11 to 36% after 12-days immersing in phosphate-buffer saline at 37°C. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: biopolymer and renewable polymer; structure–property relationship; biodegradable

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INTRODUCTION

It is widely adopted that the development of biodegradable polymers is an efficient solution for environmental issues[1–4] and the depletion of petroleum resources. [5–7] Lactic acid (LA) is an attractive monomer that can be produced from the annually renewable biomass such as corn and sugarcane. Its homopolymer, poly(lactic acid) (PLA), is completely derived from renewable resources and regarded as a promising biopolymer.[8,9] Therefore, LA-based polymers have received growing attention due to their renewable and biodegradable nature.[10–14] Currently, polymeric materials derived from renewable resources have been applied in various fields such as biomedical products and food packaging.[15–17]

Although the advantages of PLA are obvious, its application is somewhat limited by its inherent drawbacks such as brittle and hydrophobic properties.[18–21] It is known that poly(ethylene glycol) (PEG) is a water-soluble, flexible, nontoxic, and biocompatible polymer.[22] PEG is often adopted to functionalize PLA.[23] Actually, PEG is an efficient plasticizer for improving the ductility of PLA,[24–27] as well as a good block to enhance the hydrophilicity of PLA.[28,29]

To prepare a novel LA-based polymer by using LA and PEG as starting materials, we design a facile route. Seppälä et al.[30] have presented a strategy including oligomerization and chain linking to convert LA to polymer directly. They have synthesized LA-based poly(ester-urethane) (LPEU) through linking the hydroxyl-terminated oligomer with diisocyanate. Herein, we intend to generate a kind of LPEU which contains short lactate sequences and PEG segments. The target polymer is completely different from the reported LA-based polymers. In addition, our approach is different from the developed ones, and the reactions involved are easily to be carried out. We synthesize a diol precursor first through the esterification between LA and low-molecular-weight PEG. Then novel LA-based polyurethane is obtained by two-step polymerization including addition and chain extension reactions. We expect that the polymer created in this way may behave some characteristic and be suitable for temporal applications such as packaging and biomedical fields. Besides exploring the synthesis route, this article examines the effect of the chain length of PEG on the crystallization behavior and other properties of LPEU as well.

EXPERIMENTAL

Materials

LA (85% aqueous solution), PEG with number average molecular weight of 1200 and 4000 (PEG1000 and PEG4000), respectively,

Table I. Reaction Parameters of Synthesizing the Intermediates and Polymers Containing Short Lactate Sequences and Short PEG Segments

Feeding ratio (mol/mol)	Parameters							
	LA [a] (mL)	PEG1[b] (g)	PEG4[b] (g)	Yielding (%)	LPEG1K[c] (g)	LPEG4K[c] (g)	TDI[d] (mL)	BDO[e] (mL)
15:1	40	35	/	84.0	/	/	/	/
40:1	40	/	45	76.7	/	/	/	/
1:2.5:1.5[f]	/	/	/	95.2	7	/	1.56	0.58
1:2.5:1.5[f]	/	/	/	94.1	/	7	0.48	0.18
1:4.5:3.5[f]	/	/	/	94.4	7	/	2.80	1.36
1:4.5:3.5[f]	/	/	/	94.3	/	7	0.86	0.42

[a]It represents lactic acid.
[b]They represents PEG1000 or PEG4000, respectively.
[c]They represents the lactic acid-based diol derived from PEG1000 or PEG4000, respectively.
[d]It represents toluene 2,4-diisocyanate.
[e]It represents 1,4-butanediol.
[f]It is the ratio of LPEG/TDI/BDO.

toluene 2,4-diisocyanate (TDI), 1,4-butanediol (BDO), *N, N*-dimethylformamide (DMF), dibutyltin dilaurate, and diethyl ether were all analytical reagent grade, purchased domestically and used as received.

Synthesis of LA-Based Diol

LA-based oligomer diol, which was represented as LPEG hereafter, was prepared via the esterification reaction between LA and PEG with different number average molecular weight. Briefly, 40 mL (0.45 mol) LA and 35 g PEG1000 or 45 g PEG4000 was kept at 80°C for 8 h under vacuum (around 5 mmHg). The mixture was transferred into a dialysis bag (molecular weight cut off 500 g/mol), and then dialyzed against 1 L distilled water for 48 h. The distilled water was replaced every 12 h. At last, a milk-white pasty solid product was obtained by freeze-drying the residue in the bag.

Synthesis of LPEU

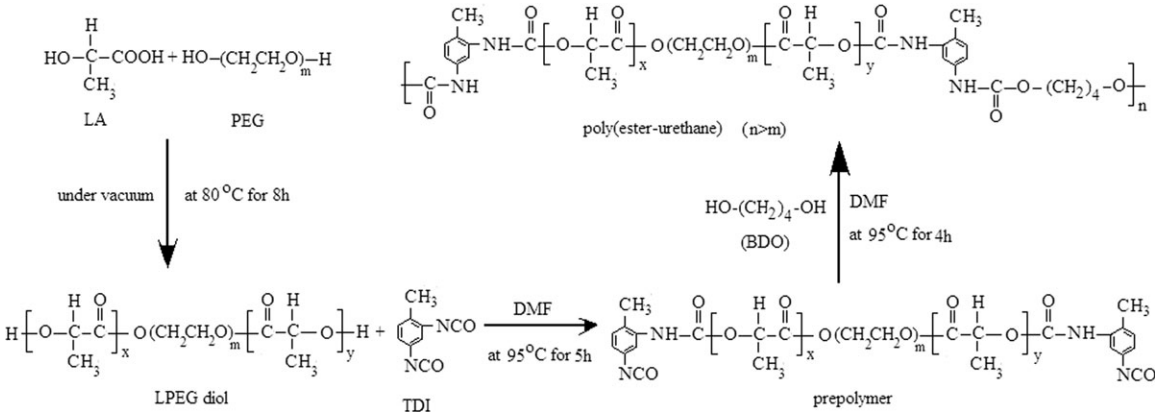
Seven grams LPEG was dissolved in 7 mL DMF with stirring under nitrogen. A predetermined amount (Table I) of TDI was slowly added into the flask and the mixture was maintaining at 95°C under agitating for 5 h. Then, an adequate amount (Table I) of BDO and 1% of dibutyltin dilaurate were supplied. The reaction was allowed to continue until no isocyanate (NCO) groups were detected. After the reaction mixture was cooled down to room temperature, the polymer was precipitated from 30 mL diethyl ether. The product, LPEU, was dried under vacuum overnight to constant weight. Similarly, a control poly(urethane) (PEGU) was obtained by replacing LPEG with PEG (PEG/TDI/BDO = 1:4.5:3.5, mol/mol) to conduct the polymerization.

Characterizations of LPEU

LPEG diol and the polymer LPEU were mixed with dry KBr and compressed into disks, respectively. Fourier transform infrared spectra (FTIR) of the samples were recorded using a Nexus 470 FTIR spectrometer (Thermo Fisher Scientific, USA).^{1}HNMR spectra of LPEG and LPEU were recorded on a Bruker AV400 NMR spectrometer (Bruker BioSpin, Rheinstetten, Germany) using tetramethylsilane and $CDCl_3$ as an internal standard and solvent, respectively. The molecular weight and distribution of the samples were measured on a Waters gel permeation chromatography (GPC, Waters Corporation, USA) with three linear Styragel columns, Waters 1515 pump, and Waters 2414 differential refractive index detector at 40°C. tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL/min and polystyrene standards were used for calibration. Thermogravimetric analyses (TGA) of the intermediate and the polymer were carried out with a TA V2.4 F thermoanalyzer (Thermo Fisher Scientific, USA). Analyses were conducted over the temperature range from 25 to 800°C with a programmed temperature increment of 10°C/min under N_2 atmosphere. X-ray diffraction (XRD) profiles of the samples were collected with a Bruker D8-Advanced diffractometer (Broker, Germany) using Nickel-filtered Cu Kα radiation (k = 0.15406 nm) and scanned from 10 to 50° at a scan speed of 3°/min. The morphology of LPEG and LPEU was observed with polarizing optical microscopy on a Leica DM2500P microscope (Leica, Germany) equipped with a video camera. The sample was placed between a microscope glass and a cover slip, and heated with a Leitz 350 hot stage. Surface wettability of PEG, LPEG, and LPEU films were estimated from the contact angle (CA) measurements with a JC-2000 C CA analyzer (Powerach, China). Static CAs of water on the samples were determined and an average of five measurements was taken. Different scanning calorimetry (DSC) analyses of the LA-based intermediate and polymer were carried out with a Netzsch DSC 200 F3 analyzer (Netzsch, Germany). The samples were heated from −100 to 150°C at a heating rate of 10°C/min to record DSC curves under nitrogen atmosphere.

In Vitro Degradation of LPEU

LPEU was dissolved in 35 wt % DMF and cast onto a silicone mould. The solvent was allowed to be evaporated for 48 h. PEGU film was obtained by polymerization directly. The formed films were dried in vacuum to constant weight and cut into 5 × 5 × 2 mm^3 tabular samples. The samples were weighed, placed in cuvettes that contained 5 mL phosphate-buffer saline (PBS, 0.1 *M*, pH 7.4), and maintained at 37°C. At timed intervals, the samples were removed, rinsed with distilled water, and dried under vacuum at ambient temperature and weighed. The weight loss percentages (WLP) were calculated as WLP (%) = $(W_0 - Wt)/W_0 \times 100$, where W_0 and W_t were the initial dry mass of samples and their dry mass at different time, respectively. An average of triplicate measurements was taken.



Scheme 1. Synthesis route of poly(ester-urethane) containing relatively short lactate sequences and short PEG segments.

RESULTS AND DISCUSSION

Synthesis of the LA-Based Intermediate and Polymer

Our goal is to prepare LPEU directly from LA and tailor its properties through a facile and efficient way. Chain linking of LA-based hydroxyl-terminated prepolymer with diisocyanate is proven to be an efficient way to produce LPEU[30] and has been applied recently.[31,32] However, long lactate sequences may bring about some limitations, such as the aforementioned brittle and hydrophobic properties of PLA.[18–21] In viewing of this, we think LA-based polymers containing short lactate sequences probably exhibit some characteristic. Accordingly, we have synthesized a LPEU which is composed of monomeric LA and ethylene oxide units.[33] But the hydrophilicity of structure units on the chain is poor. Therefore, the obtained polymer is hydrophobic enough and its degradation rate is low.

It is known that the degradability of LA-based polymers is mainly attributed to the hydrolysis of ester bonds. One practicable way to significantly accelerate the degradation of hydrophobic LA-based polymer is to incorporate hydrophilic segments onto its backbone.[34] PEG with the molar mass lower than 30,000 possesses unique physicochemical and biological properties, and is widely used to modulate the properties of degradable polyesters.[35] Thus, conjugating short PEG blocks with short lactate sequences may be an alternative strategy for constructing LPEU with controlled hydrophilicity, degradability, ductility, and other properties.

The synthesis route to achieve such a goal is illustrated in Scheme 1. First, LPEG that contain short lactate sequences and PEG segments with various lengths are prepared via the esterification between LA and PEG with molar mass of ca. 1000 and 4000, respectively. The esterification is conducted under mild conditions to reduce side reactions. Excess LA is used to ensure the esterification between LA and PEG is carried out as completely as possible. Then, the addition polymerization of LPEG and TDI with BDO as chain extender is performed. It is necessary to mention that TDI is just used to evaluate the presented route. TDI can be replaced with other diisocyanates to vary the structure and properties of LPEU. No matter what kind of diisocyanate is adopted, the obtained poly(ester-urethane) is composed of short lactate sequences and short PEG moieties. In particular, the lactate sequences in LPEU chains are much shorter than those in the reported ones obtained via chain linking.

Structure and Morphology of the LA-Based Intermediate and Polymer

To verify the synthesis route mentioned above is feasible, the structure and morphology of the obtained LA-based intermediate and polymer are analyzed with a variety of measurements. The structure of LPEG and LPEU are confirmed with FTIR and ^{1}HNMR (Figures 1 and 2). Compared to the spectra of PEG, one more characteristic absorption band appears at 1748 cm^{-1} on that of LPEG, which is attributed to the stretching vibration of carbonyl group. The characteristic peak appeared around 3470 cm^{-1} belongs to the stretching vibration of hydroxyl group. These suggest the successful conjugation of LA and PEG. As for the spectra of LPEU, it is found that the wide absorption band of —NH— group appears between 3399 and 3263 cm^{-1}, while the characteristic peaks of amide group exhibit at 1748 and 1599 cm^{-1}. These results indicate that the route of synthesizing LPEU from LA is practicable.

Figure 2 shows the difference between the ^{1}HNMR spectra of PEG and that of LPEG. The multiplet signals at 3.6 ppm are

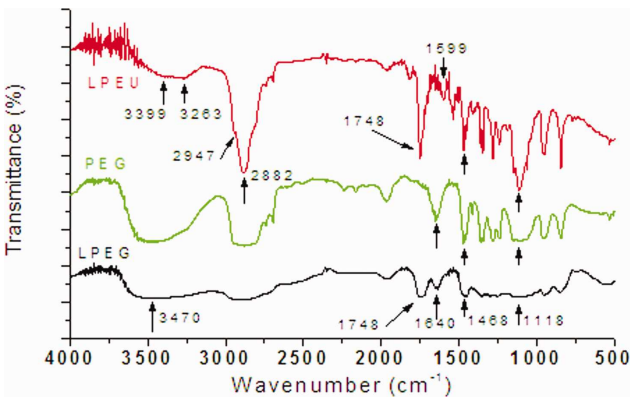


Figure 1. FTIR spectra of PEG, the LA-based diol intermediate (LPEG), and polymer (LPEU). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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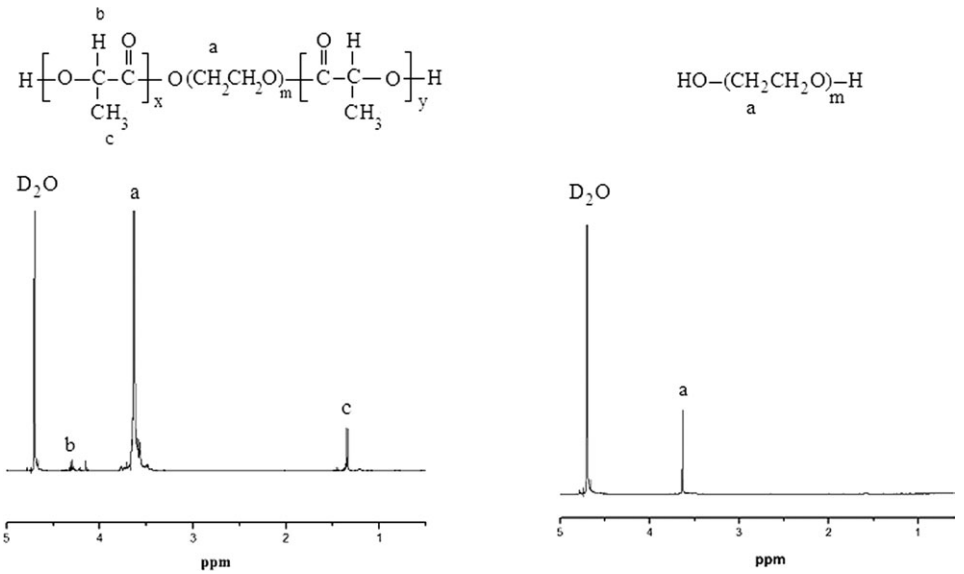

Figure 2. The ^{1}HNMR spectra of PEG and the LA-based diol intermediate (LPEG).

attributed to the protons of methylene groups of PEG or PEG segments in LPEG.[36] The protons of methine and methyl groups show their chemical shifts around 4.08 and 1.3 ppm. As shown in Figure 3, the proton of —NH— group in a urethane bond (—NH-COO—) exhibits its chemical shift at 7.0 ppm.[37] The signs at 1.3 and 4.08 ppm are related to the protons of lactate units, and 3.6 ppm for methylene groups of PEG moieties on LPEU chains. The protons on TDI residues exhibit their signs at 7.3 and 2.13 ppm. The peak appeared at 4.32 ppm is attributed to the protons of methylene groups of BDO residues. Accordingly, ^{1}HNMR analysis results also verify the structure of the LA-based polymer and its diol precursor.

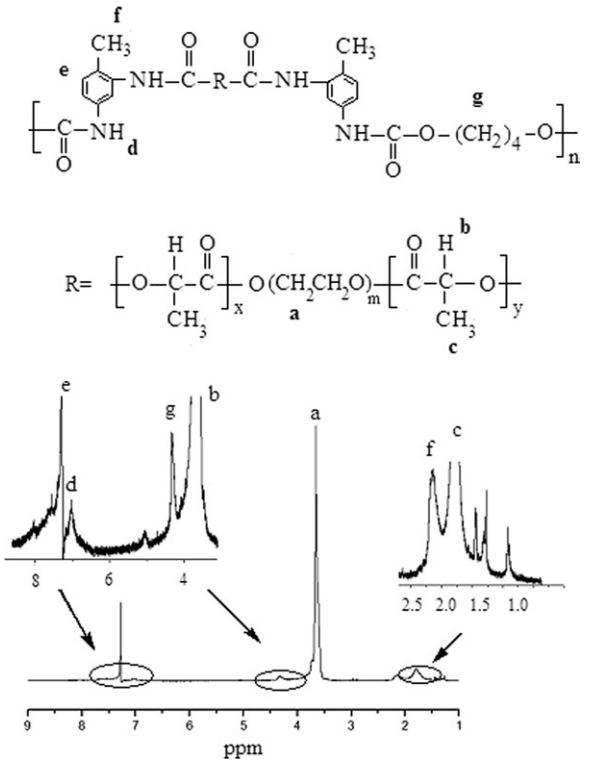

Figure 3. The ^{1}HNMR spectra of the LPEU.

GPC measurements (Table II) show that the number average molecular weight (M_n) of LPEU that derived from LPEG with different M_n is within the range of 1.0×10^4–1.8×10^4. The molar mass of the LA-based diol is slightly higher than its precursor PEG, which proves that the lactate units in LPEG molecules are as short as we expected. LPEG is purified by a dialysis process, compounds with molar mass lower than 500 are

Table II. Molecular Weights and Thermal Transition Temperatures of the Intermediates and Polymers Containing Monomeric Lactate Sequences and Short PEG Segments

Samples	M_n (g/mol)[a]	M_w (g/mol)	PDI[b]	Tm (°C)[c]	T_g (°C)[c]
LPEG1K[d]	1500	1600	1.07		
LPEG4K[d]	5200	5700	1.10	52.5	Not found
LPEU1K-25[e]	8000	8500	1.06	Not found	−25.7
LPEU4K-25[e]	15,500	15,600	1.01	51.7	Not found
LPEU1K-45[f]	9300	10,800	1.16	Not found	23.1
LPEU4K-45[f]	17,700	18,900	1.07	48.2	Not found

[a] M_n and M_w represent number and weight average molecular weight respectively, which are measured with gel permeation chromatography.
[b] PDI represents polydispersity index.
[c] both are analyzed with differential scanning calorimetry.
[d] The lactic acid-based diols derived from PEG1000 and PEG4000, respectively.
[e] The lactic acid-based polymers derived from LPEG1K and LPEG4K with the feeding molar ratio of 1:2.5:1.5 (LPEG/TDI/1,4-butanediol), respectively.
[f] The lactic acid-based polymers derived from LPEG1K and LPEG4K with the feeding molar ratio of 1:4.5:3.5 (LPEG/TDI/1,4-butanediol), respectively.

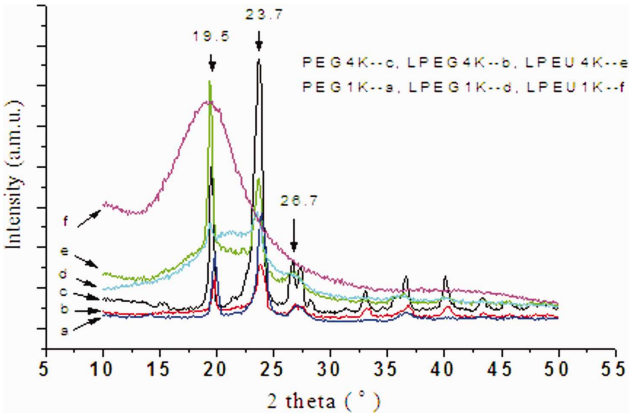

Figure 4. XRD profiles of PEG, the LA-based diol intermediate (LPEG), and polymer (LPEU) with molar mass of 1000 and 4000, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

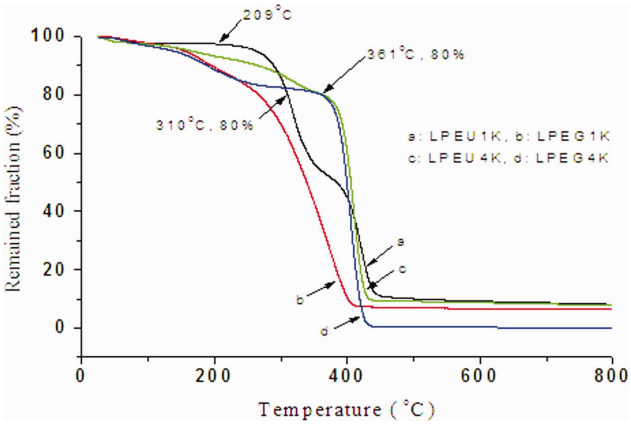

Figure 6. TGA profiles of the LA-based diol intermediate (LPEG) and polymer (LPEU) with molar mass of 1000 and 4000, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thoroughly removed. As a result, the distribution of molecular weight of intermediate is narrow. The M_n of LPEU is obviously higher than that of LPEG, which means LA-based polymer is obtained.

PEG is a semicrystalline polymer. Both the XRD patterns of PEG1000 and PEG4000 exhibit two sharp peaks around 19.5° and 23.7°, as well as several small peaks at the 2θ higher than 26.7°. There are two sharp peaks on the same positions of LPEG diols' XRD profiles, but their intensity are lower (Figure 4). These indicate the morphology of LPEG is similar to PEG, that is, both of them are crystalline. Interestingly, it is found that the LPEU prepared from LPEG with shorter PEG segments only shows one wide peak, whereas the polymer obtained from that with longer PEG segments exhibits nearly the same pattern to its precursor. Evidently, the polymer that contains longer PEG is readily to crystallize, whereas the LPEU derived from PEG of lower molar mass is amorphous. Such a morphology difference may be attributed to the short lactate sequences are linked with PEG moieties in alternative way. Thus, the crystallizability of the polymer is significantly depended on the chain length of PEG. DSC analysis results prove this once more. LPEU derived from PEG1000 exhibits a glass transition, while LPEU derived from PEG4000 only shows a melt peak (Table II). These phenomena imply the morphology of LPEU is able to be modulated with the starting materials. In addition, it is observed that both LPEG and LPEU can form spherulite (Figure 5), which is consistent with what mentioned above.

Properties of the LA-Based Polymer

For the sake of acquiring the information about the characteristic of the LA-based polymer and the relationship between the structure and the properties, we have examined the thermal stability, hydrophilicity, and degradability of LPEU samples. It is observed that the thermal stability of LPEU is higher than that of the corresponding diols. It is also found that the decomposition temperatures of LPEU obtained from PEG1000 and PEG4000 are about 310 and 361°C, respectively, at the same

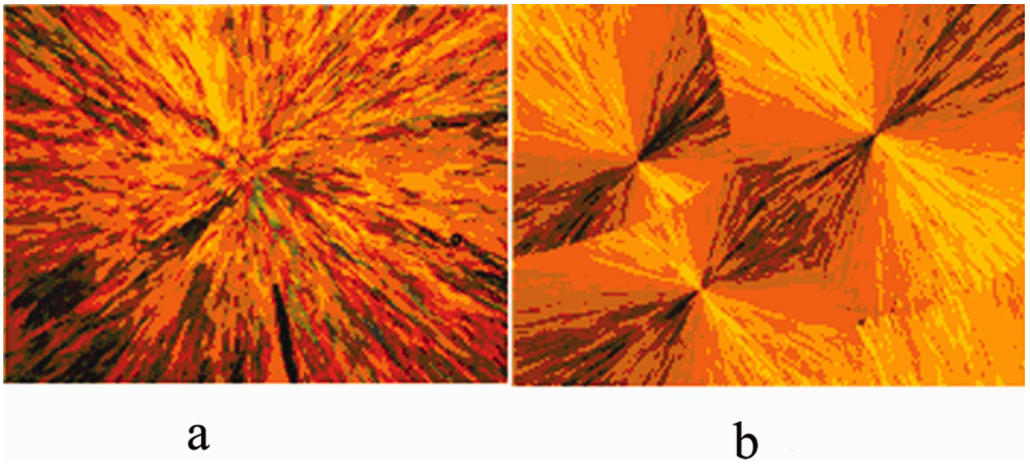

Figure 5. Polarizing optical microscopy images of the LA-based poly(ester-urethane) (LPEU, right) and the its precursor (LPEG, left) that derived from poly(ethylene glycol) 4000 at room temperature with magnification of 200. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

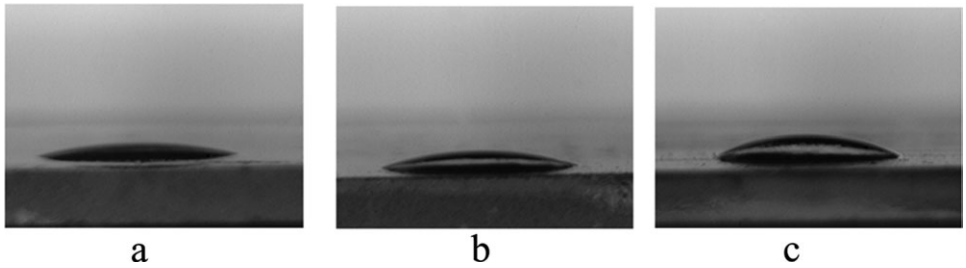

Figure 7. CAs of water on poly(ethylene glycol) with molar mass of 4000 (a), the LA-based diol (b) and poly(ester-urethane) (c).

remained fraction of 80% (Figure 6), which means that LPEU containing longer PEG segments is able to resistant higher temperature. The LA-based diol exhibits similar order of thermal stability. The dependence of thermal properties of the LA-based intermediate and polymer on the length of PEG precursor can be attributed to the contribution of the crystallizability of PEG. TGA analysis results are in good agreement with the crystallization behavior of the samples.

As mentioned above, we attempt to tailor the hydrophilic/hydrophobic property of LA-based polymer by introducing hydrophilic PEG segments. CAs of water on the surfaces of PEG4000, its corresponding diol and poly(ester-urethane) derivatives are 17°, 20.5°, and 29.5° (Figure 7), respectively. The CA value of LPEU is slightly higher than that (20.8°) of the PLA-PEG diblock copolymer derived from PEG2000, whereas much lower than the value (95°) of the LPEU containing singular LA and ethylene oxide units.[33] In other words, the measurements of water-CA support our intention.

The direct consequence of enhancing the hydrophilicity is the improvement of hydro-degradability. The *in vitro* degradation of samples is investigated by monitoring their changes in weight during immersion in PBS at 37°C. Owing to the existence of labile ester bonds and hydrophilic PEG moieties, the weight loss percentage of LPEU reaches 19.1% after 12 days' hydrolytic degradation (Figure 8). The WLP of polyurethane directly prepared from PEG is lower than 1.5% for the same duration. As for the LPEU containing singular LA and ethylene oxide units, its WLP is only 2.7% after 7 months' degradation.[33]

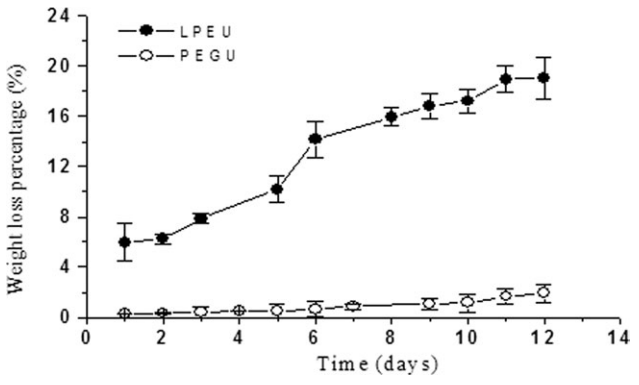

Figure 8. The *in vitro* degradation behavior of the LA-based poly(ester-urethane) (LPEU) in phosphate buffer solution of pH 7.4 at 37°C.

CONCLUSIONS

A facile strategy is designed to prepare novel LA-based poly(ester urethane) by using LA as starting material. The route includes three steps such as esterification, addition polymerization, and chain extension. These reactions are common and easily to be performed. Moreover, the structure of the tailor-made LPEU is absolutely different from the reported LPEU. The lactate sequences in the polymer chains are much shorter than those in similar polymers obtained through chain linking. As far as we know, the presented synthesis process and such a kind of LA-based polymer have not been found in the literatures.

The special structure of the prepared LA-based polymer is verified. Owing to the existence of short lactate sequences and short PEG segments, the obtained polymer shows enhanced thermal stability, hydrophilicity, and degradability. In addition, the properties of the products are able to be modulated by simply changing the starting material. The results reveal that the presented way is feasible and controllable. In addition, the structure and properties of the LA-based polymer are able to be further modified by varying the components such as replacing TDI with an aliphatic diisocyanate.

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