

# Chain extension and branching of poly(L-lactic acid) produced by reaction with a DGEBA-based epoxy resin

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Received 12 August 2007; accepted in revised form 20 September 2007

**Abstract.** Dicarboxylated poly(L-lactic acid) (PLLA) was synthesized by reacting succinic anhydride with L-lactic acid prepolymer prepared by melt polycondensation. PLLA and epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) copolymers were prepared by chain extension of dicarboxylated PLLA with DGEBA. Infrared spectra confirmed the formation of dicarboxylated PLLA and PLLA/DGEBA copolymer. Influences of reaction temperature, reaction time, and the amount of DGEBA on the molecular weight and gel content of PLLA/DGEBA copolymer were studied. The viscosity average molecular weight of PLLA/DGEBA copolymer reached 87 900 when reaction temperature, reaction time, and mol ratio of dicarboxylated PLLA to DGEBA is 150°C, 30 min, and 1:1 respectively, while gel content of PLLA/DGEBA copolymer is almost zero.

**Keywords:** biodegradable polymers, poly(L-lactic acid), epoxy resin, copolymers

## 1. Introduction

Poly(L-lactic acid) (PLLA) is a completely biodegradable and well biocompatible aliphatic polyester [1]. PLLA has many potential applications in packaging and consumer goods due to its excellent mechanical properties, transparency, compatibility, and biosafety [2, 3].

There are generally two ways to synthesize PLLA, ring-opening polymerization and direct polycondensation [4]. Ring-opening polymerization requires highly purified L-lactid, which makes PLLA rather expensive, hardly competitive with current polymers [5, 6]. Direct melt polycondensation can simplify the synthetic process and reduces the cost of PLLA. However, it is difficult to prepare PLLA with high molecular weight by direct polycondensation because of the complicated equilibrium among lactic acid, H<sub>2</sub>O, L-lactid and PLA during the process [7]. The unfavorable reaction equilibrium constant makes the PLLA molecular weight in

order of only  $\sim 10^4$  g/mol. Such low molecular weight PLLA is too brittle to be used as a useful material [8]. PLLA should have at least  $\sim 10^5$  g/mol order of molecular weight to exhibit an acceptable level of mechanical properties [9]. Increasing of the molecular weight of PLLA is imperatively demanded [8].

The low molecular weight PLLA synthesized by direct melt polycondensation has reactive functional groups such as hydroxyl and carboxyl group, and its molecular weight can be improved through chain extension. Woo *et al.* [10] used hexamethylene diisocyanate (HDI) as chain extender, and the average molecular weight of PLLA was improved to 76 000. Kylma and Seppala [11] prepared hydroxyl-terminated PLLA oligomer, used HDI as chain extender, and got the poly(ester-urethane) elastomer. Zhou *et al.* [12] first synthesized telechelic poly(ethylene glycol) (PEG) by reacting PEG with isophorone diisocyanate (IPDI), then

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prepared PLLA/PEG multiblock copolymers by coupling reactions between PEG telechelic oligomer and L-lactic acid prepolymer. The elongation at break of the resulting copolymer can reach 320%. Cohn *et al.* [13] synthesized a series of poly(ethylene oxide)/poly(L-lactic acid) multiblock poly(ether-ester-urethane)s using HDI as extender. It is obvious that isocyanate is widely used as chain extender. However, it has high volatility and toxicity. This will do harm to experiments and pollutes the environment.

Huh *et al.* [14] first synthesized PLLA with carboxylated end-groups by direct polycondensation, then prepared PEG/PLLA copolymer by polycondensation reaction between PEG and PLLA. This is a new method to increase the molecular weight of PLLA. However, the method requires the presence of solvent and further purification of the products. In addition, the chain extension requires long reaction time.

In this paper a DGEBA-based epoxy resin, which has nearly no volatility and toxicity was used to extend the carboxyl-terminated PLLA in short reaction time in melt, and resulting in high molecular weight products. This method avoids the shortages of the previous techniques and has rarely been reported in published articles so far.

## 2. Experimental

### 2.1. Materials

L-lactic acid (85 wt%, L-lactic acid content: 98–99%) was purchased from Purac Biochem Co. (Holland). The impurity was removed before use

by distillation under reduced pressure at 130°C for about 2 h.

Stannous octoate ( $\text{Sn}(\text{Otc})_2$ ), succinic anhydride, p-toluenesulfonic acid monohydrate (TSA), tetrahydrofuran (THF), acetone, tetrabutylammonium bromide (TBAB), and DGEBA-based epoxy resin (226.2 g/mol epoxy groups) were obtained from Shanghai Chemicals, and used as received without further treatment.

### 2.2. Preparation of dicarboxylated PLLA

The melt polycondensation of L-lactic acid was carried out in a rotavapor equipped with a thermostated oil bath. The rotation speed was 120 rpm. 200 g purified L-lactic acid, 0.5 wt% catalyst  $\text{Sn}(\text{Otc})_2$  and 0.5 wt% co-catalyst TSA were put into a 500 ml round-bottom flask. The reaction temperature was gradually raised from 150 to 180°C and the pressure was lowered from 5000 to 100 Pa. After a total reaction time of about 12 h the L-lactic acid prepolymer was obtained. Then, the desired amount of succinic anhydride was added to the flask. The reaction of succinic anhydride with L-lactic acid prepolymer was carried out at 180°C and 100 Pa for 1 h. The molten polymer was poured into a stainless steel pan and placed in a desiccator to cool down. The dicarboxylated PLLA, with a viscosity average molecular weight of 10 070, was obtained.

### 2.3. Chain extension reaction

The chain extension reaction of dicarboxylated PLLA with DGEBA was also carried out in rotava-

**Table 1.** Experimental conditions for chain extension reaction<sup>a</sup>

Series	Run number	PLLA [g]	DGEBA [g]	TABA [g]	Reaction time [min]	Reaction temperature [°C]
A	A1	73.7	12.0	0.86	30	140
	A2	73.7	12.0	0.86	30	150
	A3	73.7	12.0	0.86	30	160
	A4	73.7	12.0	0.86	30	170
	A5	73.7	12.0	0.86	30	180
B	B1	61.4	10.0	0.71	10	150
	B2	61.4	10.0	0.71	20	150
	B3	61.4	10.0	0.71	30	150
	B4	61.4	10.0	0.71	40	150
C	C1	70.0	5.7	0.70	30	150
	C2	70.0	7.6	0.70	30	150
	C3	70.0	11.4	0.70	30	150
	C4	70.0	17.1	0.70	30	150

<sup>a</sup>Pressure, 100 Pa in series A, B and C

por. The rotation speed was 150 rpm. The predetermined amount of dicarboxylated PLLA, DGEBA and TBAB catalyst were put into a 500 ml round-bottom flask. The reaction was performed at 100 Pa and desired temperature and time. Chain extension reaction conditions for all the series of experiments are summarized in Table 1.

#### 2.4. Analysis and characterization

The amount of carboxyl group in L-lactic acid prepolymer and dicarboxylated PLLA was determined as following steps. 0.20 g sample was dissolved in 40 ml THF, and then titrated by 0.1 mol/l NaOH ethanol solution using phenolphthalein as indicator. The amount of carboxyl group (AC) is given by Equation (1):

$$AC \text{ [mol/g]} = \frac{(V_1 - V_0) \cdot 10^{-3} \cdot C}{m} \quad (1)$$

where  $V_0$  the amount of NaOH consumed by using THF as reference [ml],  $V_1$  is the amount of NaOH consumed by sample [ml],  $C$  is the mol concentration of titration solution [mol/l],  $m$  is the weight of sample [g].

The gel content (GC) of PLLA/DGEBA copolymer was determined by extraction. The rough sample was extracted by THF using Soxhlet extractor. The crosslinked copolymer, which remained in extractor, was dried to constant weight in vacuum oven at 80°C. The uncrosslinked copolymer was extracted from the rough sample by THF. The GC is given by Equation (2):

$$GC \text{ [%]} = \frac{m_2}{m_1} \cdot 100 \quad (2)$$

where  $m_1$  is the weight of rough sample [g] and  $m_2$  is the weight of crosslinked copolymer [g].

The viscosity average molecular weight of dicarboxylated PLLA and uncrosslinked PLLA/DGEBA copolymer was measured by the intrinsic viscosity method. The viscosity was determined in THF at 30°C by using a viscometer. The intrinsic viscosity was calculated from the equation of Rongshi Cheng [15], given by Equation (3). The Mark-Houwink equation is given by Equation (4) [16]:

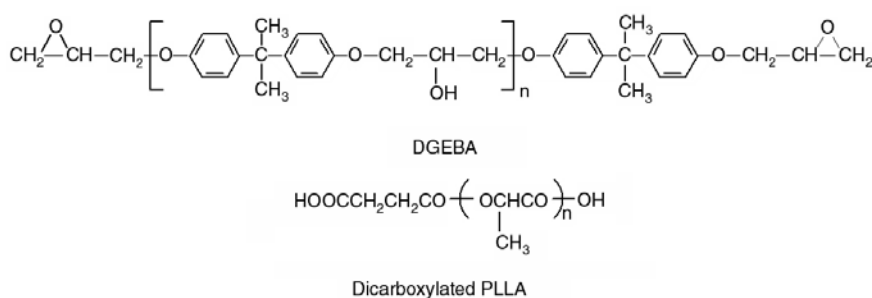
$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{c} \quad (3)$$

$$[\eta] = 1.29 \cdot 10^{-4} \bar{M}_V^{0.82} \quad (4)$$

Infrared spectroscopic information of polymers was obtained using Spectrum 100 Fourier Transform Infrared spectrophotometer (PE Corp. USA).

#### 3. Reaction mechanism

The chemical structures of DGEBA and dicarboxylated PLLA are shown in Figure 1. Synthesis of PLLA/DGEBA copolymers involves following steps: (1) Melt polycondensation of L-lactic acid to prepare L-lactic acid prepolymer. (2) L-lactic acid prepolymer reacting with succinic anhydride to prepare dicarboxylated PLLA. (3) Dicarboxylated PLLA reacting with DGEBA to prepare PLLA/DGEBA copolymers. The epoxy-acid reaction is complex in the presence of TABA [17]. The reaction mechanism of dicarboxylated PLLA reacting with DGEBA may be described as Figure 2. The linear molecule is obtained as reaction I, while the ester formed by the epoxy-acid reaction can react with the OH groups through a transesterification reaction as reaction II. The reaction II leads to chain branching and gel formation.



**Figure 1.** Chemical structures of DGEBA and dicarboxylated PLLA

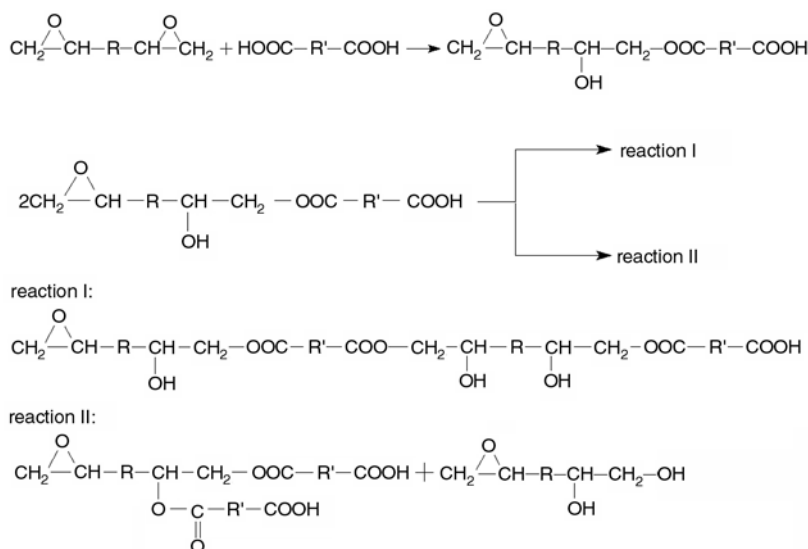


Figure 2. The reaction mechanism of dicarboxylated PLLA reacting with DGEBA

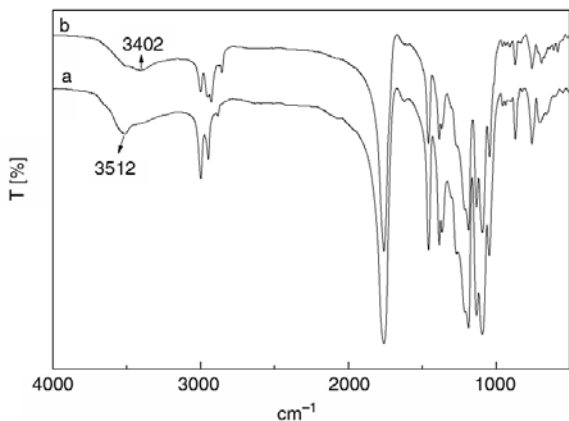


Figure 3. IR spectra of L-lactic acid prepolymer and dicarboxylated PLLA. (a) L-lactic acid prepolymer; (b) dicarboxylated PLLA

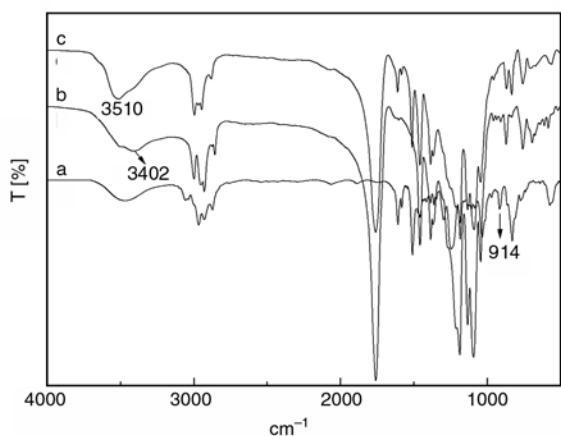


Figure 4. IR spectra of dicarboxylated PLLA, DGEBA and PLLA/DGEBA copolymer. (a) DGEBA; (b) dicarboxylated PLLA; (c) PLLA/DGEBA copolymer

## 4. Results and discussion

### 4.1. Evidence of reaction

Figure 3 shows the infrared spectra of L-lactic acid prepolymer and dicarboxylated PLLA. The absorbance at 3512 cm<sup>-1</sup> in Figure 3 (a) indicates the terminal -OH of L-lactic acid prepolymer. The absence of 3512 cm<sup>-1</sup> in Figure 3 (b) indicates that the terminal -OH of L-lactic acid prepolymer was transformed to terminal -COOH of dicarboxylated PLLA (3402 cm<sup>-1</sup>). The amount of carboxyl group of L-lactic acid prepolymer and dicarboxylated PLLA is 3.7·10<sup>-4</sup> and 7.2·10<sup>-4</sup> mol/g, respectively. The infrared spectra of dicarboxylated PLLA, DGEBA and PLLA/DGEBA copolymer are shown in Figure 4. The absorbance at 914 cm<sup>-1</sup> in Figure 4 (a) and 3402 cm<sup>-1</sup> in Figure 4 (b) indicates the terminal epoxy group of DGEBA and carboxyl group of dicarboxylated PLLA, respectively. The appearance of new absorbance at 3510 cm<sup>-1</sup> and absence of 914 cm<sup>-1</sup>, 3402 cm<sup>-1</sup> in Figure 4 (c) indicates that the epoxy group of DGEBA and carboxyl group of dicarboxylated PLLA was transformed to hydroxyl group of PLLA/DGEBA copolymer.

### 4.2. Effect of reaction temperature

Figure 5 shows the effect of reaction temperature on the  $\bar{M}_v$  of uncrosslinked PLLA/DGEBA copolymer and gel content of PLLA/DGEBA copolymer. The experimental conditions are shown in series A of Table 1. The mol ratio of dicarboxylated PLLA

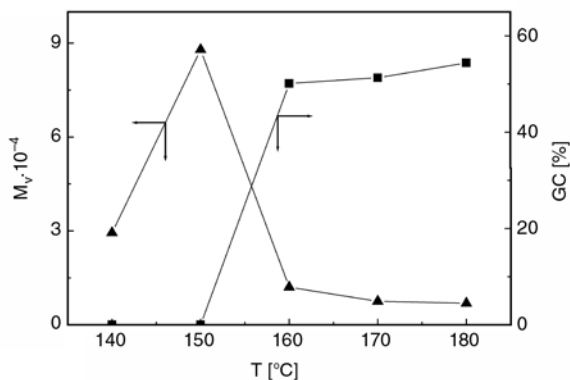


Figure 5. Effect of reaction temperature on chain extension reaction

to DGEBA is 1:1. Figure 5 reveals that the  $\bar{M}_V$  of uncrosslinked PLLA/DGEBA copolymer is the highest when the reaction temperature is 150°C. The gel content of PLLA/DGEBA copolymer is almost zero when temperature is lower than 150°C, it increases rapidly with increasing reaction temperature during 150–160°C, and after that it changes indistinctively. The transesterification reaction (reaction II) is more difficult than that of linear reaction (reaction I) in Figure 2, as a result, no gel content was observed at low temperature. The reaction of transesterification reaction increased considerably when reaction temperature increased, so the gel content of PLLA/DGEBA copolymer increased with increasing reaction temperature.

#### 4.3. Effect of reaction time

Figure 6 shows the effect of reaction time on the  $\bar{M}_V$  of uncrosslinked PLLA/DGEBA copolymer and gel content of PLLA/DGEBA copolymer. The experimental conditions are shown in series B of Table 1. The mol ratio of dicarboxylated PLLA to

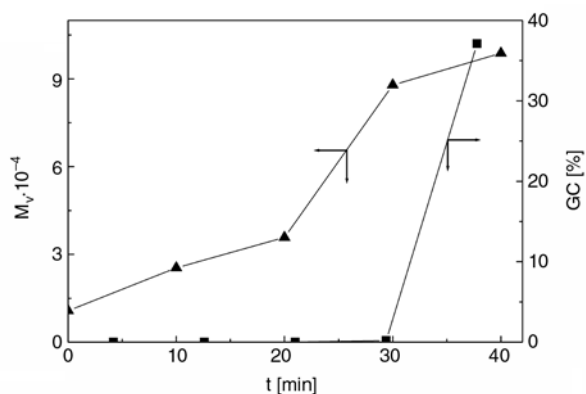


Figure 6. Effect of reaction time on chain extension reaction

DGEBA is also 1:1. The  $\bar{M}_V$  of copolymer increases steadily with increasing reaction time. However, the gel content is almost zero during the beginning 30 minutes, and after that it increases rapidly with increasing reaction time. When the reaction time reaches 40 min, the gel content of the copolymer is 37.1%. The copolymer will be difficult to process when gel content is high. So, the best reaction time is 30 min.

#### 4.4. Effect of the amount of DGEBA

The effect of the amount of DGEBA on the  $\bar{M}_V$  of PLLA/DGEBA copolymer is shown in Figure 7. The experimental conditions are shown in series C of Table 1. No gel content is observed in this reaction system which can be explained by Figure 5 and Figure 6. The  $\bar{M}_V$  of PLLA/DGEBA copolymer reaches 87 900, which is the highest, when the amount of DGEBA is 11.4 g. On this point, the feed mole ratio of dicarboxylated PLLA to DGEBA is 1:1. At other points, the amount of carboxyl group and epoxy group is not equal, which causes inadequate reaction of dicarboxylated PLLA with DGEBA.

### 5. Conclusions

PLLA/DGEBA copolymers were successfully synthesized by chain extension of dicarboxylated PLLA with DGEBA-based epoxy resin. The viscosity average molecular weight of PLLA/DGEBA copolymer reached 87 900 when reaction temperature, reaction time, and mol ratio of dicarboxylated PLLA to DGEBA is 150°C, 30 min, and 1:1, respectively; while gel content of PLLA/DGEBA copolymer is almost zero.

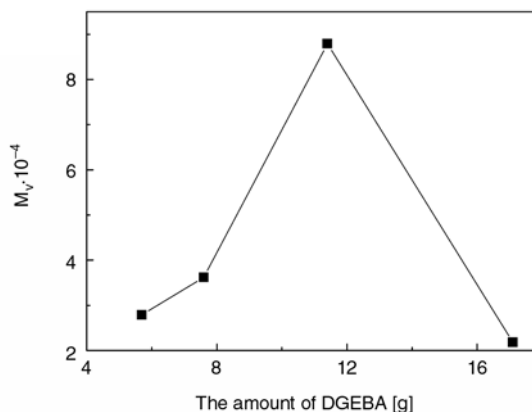


Figure 7. Effect of the amount of DGEBA on chain extension reaction



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