

H-NMR Spectroscopy Analysis of Homo and Copolymers of *L*-lactic Acid

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Abstract: A direct polymerization process was developed to synthesize homo- and copolymers of *L*-lactic acid. The properties and structures of the products were characterized by ¹H nuclear magnetic resonance (¹H-NMR). It was found that PLLA can be prepared by direct synthesis using melt polycondensation. Moreover, the number-average molecular weight (\overline{M}_n) and compositions of each polymer was determined by ¹H-NMR spectra. In the meantime, the ¹H-NMR spectra was also used for racemization analysis..

Keywords: Poly(lactic acid), ¹H nuclear magnetic resonance, number-average molecular weight, racemization.

1. Introduction

Lactic acids (LA) present in carbohydrate metabolism in nature consist of two optical isomers, *L*-lactic acid (*L*-LA) and *D*-lactic acid (*D*-LA), while racemic *D*, *L*-lactic acid (*D,L*-LA) containing equimolar *L*-LA and *D*-LA. Aliphatic polyesters derived from lactic acids are expected to have a wide promising application from biomedical materials to biodegradable plastics because of their processable, biocompatible, degradable, and excellent mechanical properties [1]. Poly(*D*-lactic acid) (PDLA), poly(*L*-lactic acid) (PLLA), and poly(*D,L*-lactic acid) (PDLLA) have been applied to biomedical materials as suture and drug delivery systems. Moreover, copolymerization of LA with various hydroxy-acids or lactones such as GA, glycolide, and ϵ -caprolactone has been performed to obtain copolyesters for different applications [2-5].

In our former studies, Homo- and copolymers of LA such as PLLA, poly(*D,L*-lactic acid) (PDLLA) and poly(*L*-lactic acid -co- glycolic acid) (PLGA) can be prepared via direct synthesis. ¹H nuclear magnetic resonance is a very useful method to analyze the properties and structures of polymers. In present work, ¹H -NMR was used in the characterization of PLLA, racemization of PLLA, the number-average molecular weight (\overline{M}_n) and compositions of each polymer.

2. Methods

A series of homo- and copolymers of *L*-lactic acid were prepared according to our former studies [3].

PLGA (90/10) was prepared from the mixture of *L*-LA/GA (90/10) (molar ratio of *L*-LA/GA being 90/10), while PLGA (70/30) from *L*-LA/GA (70/30). *D*, *L*-lactic acid (50/50) and *L*-lactic acid were utilized to synthesize PDLLA and PLLA, respectively.

¹H-NMR spectra was carried out at a temperature of 300K on a Bruker DMX-500 nmr spectrometer. All polymer samples were dissolved in deuterated chloroform with tetramethylsilane as an internal standard. Chemical shifts in ppm were referenced relatively to chloroform at 7.26 ppm in ¹H-NMR spectra. ¹H-NMR spectra were acquired as 1 % solution at 500 MHz.

3. Results and discussion

3.1 Characterization of PLLA

The typical ¹H-NMR spectra of PLLA are given in Fig. 1. The spectra of PLLA are identical with references, which show that PLLA can be prepared by direct synthesis using melt polycondensation. In ¹H-NMR spectra of PLLA and PDLLA the peaks around 5.1-5.3 ppm are due to the methine protons in LA repeat units, while the signals due to methine protons in the end groups of the polymers appear at 4.4 ppm. The peaks around 1.6 ppm are owing to methyl protons, which often interfere with those of residual lactic acid monomer [6-8].

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JFBI Vol. 2 No. 2 2009 doi:10.3993/jfbi09200910

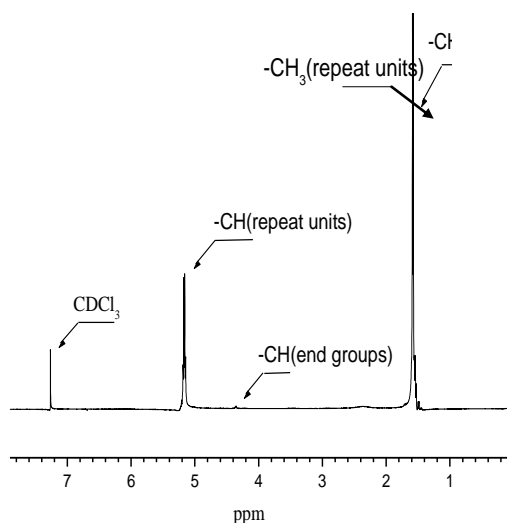


Figure 1 The typical $^1\text{H-NMR}$ spectra of PLLA.

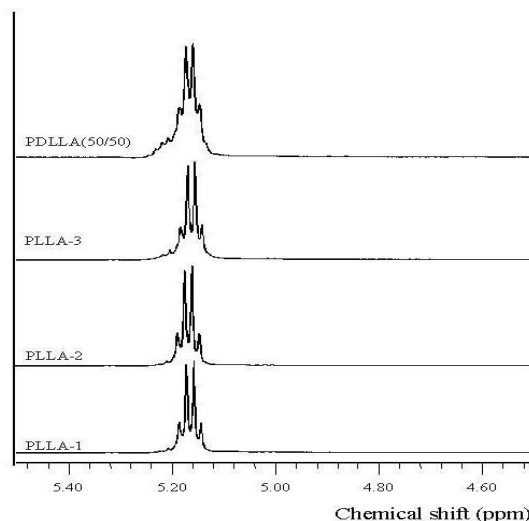


Figure 2 $^1\text{H-NMR}$ spectra of PLLA and PDLLA.

3.2 Racemization of PLLA

The $^1\text{H-NMR}$ spectra is usually used for the microstructure analysis. Racemization can reduce L-LA block lengths, which will lead to lower crystallinity and imperfect crystalline structure of PLLA. PDLLA (50/50) was considered to possess more or less racemic structure [3-5]. Fig. 2 shows the typical $^1\text{H-NMR}$ spectra of PLA in the methine region at 5.1-5.3 ppm. The methine region at 5.15 ppm in $^1\text{H-NMR}$ spectrum of PDLLA (50/50) shows two indistinctly resolved quartets caused by racemic LA units [3-5], while the spectrum of PLLA-1 shows a less intense quartet in down-field at methine region because of slight racemization of L-LA units, and so does PLLA-2 spectrum. In PLLA-3 spectrum enhanced racemization in down-field caused by long reaction time can be observed.

The CH signals in $^1\text{H-NMR}$ spectra of PLGA are similar to that of PDLLA (50/50), as shown in Fig. 3. PLGA possesses more racemic structure than PLLA-2. Furthermore, racemization of PLGA increases greatly with increasing GA fraction. The results of racemization are listed in Table 1.

Table 1 The racemization of PLLA

Samples	Racemization (%)
PLLA-1	5.8 ± 0.2
PLLA-2	6.8 ± 0.2
PLLA-3	22.7 ± 0.7
PDLLA (50/50)	50 ± 2.0

3.3 Molecular weights of polymers

The number-average molecular weight (\overline{Mn}) of each polymer was determined by $^1\text{H-NMR}$ spectra. In $^1\text{H-NMR}$ spectra of PLLA, PLGA and PDLLA, the peaks around 5.15 ppm are due to the methine protons in LA repeat units, and peaks at 4.35 ppm due to the same protons in the end groups of the polymer [4]. The peaks at 4.6-4.9 ppm are owing to methylene protons of GA blocks. Fig. 3 shows typical $^1\text{H-NMR}$ spectra obtained from PLLA-1, PLLA-2, PDLLA (50/50), PLGA (90/10), and PLGA (70/30). The \overline{Mn} s of PLLA, PLGA and PDLLA were measured by comparing the integrated area of peaks at 5.15 ppm with that at 4.35 ppm. The peaks at 1.6 ppm owing to methyl protons were not used because it often interferes with residual lactic acid monomer.