Journal of Molecular Structure 1124 (2016) 256–261

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Variable-temperature Fourier-transform infrared studies of poly(L-lactic acid) in different states of order: A 2DCOS and PCMW2D analysis☆

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ARTICLE INFO

Article history:
Received 20 August 2015
Received in revised form
19 October 2015
Accepted 27 October 2015
Available online 31 October 2015

Keywords:
Poly(L-lactic acid)
Variable-temperature Fourier-transform infrared (FT-IR) spectroscopy
Two-dimensional correlation spectroscopy (2DCOS) and perturbation-correlation moving-window two-dimensional (PCMW2D) analyses
State of order

ABSTRACT

Variable-temperature Fourier-transform infrared (FT-IR) spectra of a predominantly amorphous and a semi-crystalline poly(L-lactic acid) (PLLA) film were measured between 30 °C and 170 °C in order to investigate their temperature-dependent structural changes as a function of the initial state of order. For an in-depth analysis of the spectral variations in the carbonyl stretching band region (1803–1722 cm^{-1}) two-dimensional correlation spectroscopy (2DCOS) and perturbation-correlation moving-window two-dimensional (PCMW2D) analyses were applied. Significant spectral changes were observed during heating of the amorphous PLLA sample whereas the semi-crystalline specimen showed only slight band shifts as a function of the external perturbation. The PCMW2D results suggested that for efficient 2DCOS analyses the heating process should be split up in two temperature intervals. These analyses then provided information on the recrystallization of the amorphous regions, the presence of an intermediate state of order and a sequence scenario for the observed spectral changes.

1. Introduction

Poly(lactic acid) has attracted considerable attention because of its biodegradability, biocompatibility, and processability [1]. The source, lactic acid, can be derived from bacterial fermentation of a number of renewable agricultural products, such as corn and potato, for example. In recent years, PLA has been extensively used in the packaging industry [2,3], or as a blending component to improve the mechanical properties of other biopolymers [4,5]. It has also been applied in biomedical fields, including surgical suture [6], drug delivery systems [7] and tissue engineering [8,9]. However, the mechanical properties, the processability and the crystallization behavior of PLA strongly depend on its stereochemical structure, that can be controlled by the polymerization of varying amounts of D-lactide, L-lactide or *meso*-lactide [1,10].

In the present study variable-temperature FT-IR spectroscopy in combination with generalized 2DCOS and PCMW2D analyses were used to study the structural changes of PLLA in different initial states of order between room temperature up to the melting point. Specifically, the spectral variations in band shape and band position of the ν(C=O) carbonyl band of an amorphous and a subsequently annealed, semi-crystalline PLLA film were investigated.

Generalized 2DCOS was proposed by Noda [11] to evaluate the dynamic changes of spectra under the influence of an external perturbation and has since then been applied in a broad range of applications [12–15]. It results in a pair of synchronous and asynchronous 2D correlation spectra, which represent the overall similarity or coincidental trends and dissimilarity or out-of-phase character between two separate intensity variations measured at different spectral variables, respectively. Furthermore, 2DCOS can efficiently resolve overlapped bands and identify the sequential changes of different absorption bands characterizing specific structural subunits. PCMW2D was developed by Morita [16] on the basis of the generalized 2DCOS and the conventional moving-

☆ Dedicated to Prof. Dr. Isao Noda on the occasion of his 65th birthday.

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http://dx.doi.org/10.1016/j.molstruc.2015.10.090
0022-2860/

window techniques [17]. By introducing the perturbation variable into the correlation equation, PCMW2D is particularly suitable to monitor the spectral variations along the perturbation direction.

2. Experimental

2.1. Preparation of PLLA film

A few milligrams of poly(L-lactic acid) (PLLA) sample (NatureWorks LLC, Minnesota, USA) containing 10% of *meso*-form were dissolved in chloroform. An amorphous film sample with a thickness of 5–7 μm was prepared by casting the solution onto a surface-roughened glass plate and subsequent evaporation of the solvent at room temperature. Based on preceding DSC results (see below) a semi-crystalline film was prepared by annealing part of the as-prepared amorphous film at 145 °C for 5 h.

2.2. Variable-temperature FT-IR measurements

For the variable-temperature FT-IR measurements the samples were mounted in a specifically designed sample holder and the experimental temperature was controlled with a High THC-15 unit (Yokohama, Japan) (Fig. 1a and b). Spectra were recorded between 30 and 170 °C in intervals of approximately 10 °C. For temperature equilibration a time interval of 5 min was allowed between reaching the nominal value and recording the spectrum.

Transmission spectra were measured on a Bruker IFS 28 FT-IR spectrometer equipped with a liquid-nitrogen cooled mercury cadmium telluride (MCT) detector and 128 scans were co-added with a spectral resolution of 4 cm^{-1} and a zero-filling factor of 2.

2.3. Differential scanning calorimetry (DSC)

DSC measurements were performed on a DSC 204 F1 Phoenix system (Netzsch, Selb, Germany) over a range of 30–250 °C with a heating rate of 10 °C/min.

2.4. Generalized 2DCOS and PCMW2D analyses

Before performing the analyses, the FT-IR spectra were baseline corrected in the ν(C=O) wavenumber range (1803–1722 cm^{-1}). Then, the series of FT-IR spectra of both PLA samples were converted to comma-separated value (csv) format files and subsequently integrated into one csv file according to the requirement of the 2D*shige* software (http://sci-tech.ksc.kwansei.ac.jp/~ozaki/). Both 2DCOS and PCMW2D analyses were carried out using 2D*shige*. A window size of 3 ($2m + 1 = 3$) was chosen to guarantee a high-quality PCMW2D map. Finally, the contour maps of PCMW2D were plotted by the Origin software 6.1 (OriginLab, Northampton, MA, USA).

3. Results and discussion

In order to understand the thermal behavior of PLLA in different states of order, DSC curves were first measured (Fig. 2a and b). The amorphous PLLA shows two endothermic signals at 71.5 °C and 175 °C, corresponding to the glass transition (T_g) and the melting process, respectively. The exothermic peak at 114 °C (range from 90 to 145 °C) was caused by recrystallization of the initially amorphous PLLA during heating. In contrast, the semi-crystalline PLLA only shows a melting endotherm at 182 °C. From their respective melting enthalpies and the reference value for purely crystalline PLLA ($\Delta H_{100\%\ cryst\ PLA} = 93.7$ J/g [1]), the degree of crystallinity of the two samples was calculated to be 10.0% and 40.4%, respectively.

It needs to be emphasized that due to thickness limitations the samples used for subsequent variable-temperature FT-IR experiments were not the ones used in the DSC measurements. However, comparison of the attenuated total reflection (ATR) spectra (after correction to transmission spectra) of the samples used for the DSC investigations with the transmission spectra of the samples used for the variable-temperature FT-IR measurements indicated the same degree of crystallinity for the amorphous sample and a slightly higher state of order for the semi-crystalline sample.

Variable-temperature FT-IR spectroscopy is a frequently used technique to study structural changes of polymers as a function of temperature [18–20]. In the present study, FT-IR spectra series of the predominantly amorphous and the semi-crystalline PLLA sample have been measured between 30 °C–170 °C and are represented for the ν(C=O) wavenumber region in Fig. 3. These spectra series show marked differences not only in the carbonyl region but also in the other state of order sensitive wavenumber ranges. While for the amorphous PLLA significant changes in band position, band shape, and band intensity occur at about 90 °C (Fig. 3a), no such changes are obvious in the spectra of the semi-crystalline PLLA sample (Fig. 3b). Interestingly, however, the spectra measured at 170 °C for the two different PLLA samples are very similar. Thus, the thermal treatment of the originally amorphous sample during the FT-IR measurements leads to large structural changes whereas the heat treatment does not considerably affect the initial structure of the semi-crystalline polymer. These findings are in complete agreement with the DSC investigations where the amorphous sample undergoes considerable

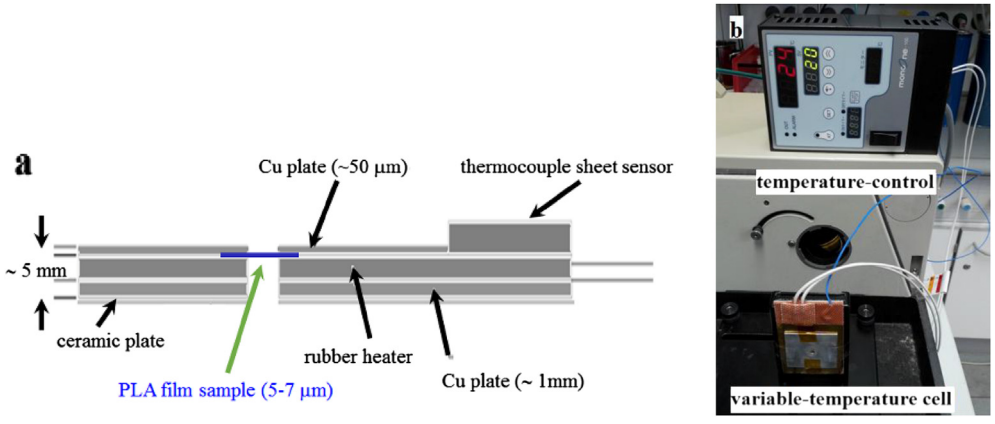

Fig. 1. (a) Schematic illustration of the sample holder and (b) photo of the variable-temperature FT-IR measurement set-up.