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Crystal polymorphism of poly(L-lactic acid) and its influence on thermal properties

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ABSTRACT

The influence of crystal polymorphism on the thermal properties of poly(L-lactic acid) (PLLA) is discussed in this contribution. Crystallization of PLLA at high temperatures yields the stable α form, whereas at low temperatures the metastable α′ modification develops, which is characterized by slightly larger lattice dimensions compared to the α counterpart, and by some degree of conformational disorder. Quantitative analysis with conventional and temperature-modulated calorimetry revealed a three-phase structure of PLLA composed of a crystal phase and two amorphous fractions with different mobility, for all the analyzed thermal histories. A higher coupling of the amorphous chain segments with the crystal phase was found in the presence of α crystals, probably due to the slightly larger lattice dimensions and the looser arrangements of PLLA chains in the α′ structure. Some peculiarities in the thermal behavior were rationalized, like an unusual frequency-dependence of the reversing apparent heat capacity upon the solid–solid transition from the α′ to the α crystals. Devitrification of the rigid amorphous segments seems also to be differently affected by the coupled crystal structure for the two analyzed crystal modifications of PLLA.

1. Introduction

Poly(L-lactic acid) (PLLA) is a biodegradable and biocompatible polyester that can be produced by renewable resources, like corn. Being non-toxic to human body, PLLA is used in biomedical applications, like surgical sutures, bone fixation devices, or controlled drug delivery. Moreover, the good mechanical properties and easy of processability make PLLA a good candidate to substitute petroleum-based polymers in selected and commodity application, with the added value of biodegradability.

Similar to other biodegradable polyesters, PLLA displays crystal polymorphism, as three main different crystal modifications can develop, named α, β, and γ forms, depending on preparation conditions. The α form of PLLA grows upon melt or cold crystallization, as well as from solution. The α form has two antiparallel chains in a left-handed 10_3 helical conformation (or distorted 10_3 helix) packed in an orthorhombic (or pseudo-orthorhombic) unit cell with $a = 1.066$ nm, $b = 0.616$ nm, $c = 2.888$ [1–3]. Hot-drawing melt-spun or solution-spun PLLA fibers to a high-draw ratio leads to the β form. An orthorhombic unit cell with six chains in the 3_1 helical conformation, with axes $a = 1.031$ nm, $b = 1.821$ nm and $c = 0.900$ nm was first proposed for the β modification [4]. Similar to α crystals, the molecular chains of the β form crystals have a nearly hexagonal packing, as the b/a is very close to $\sqrt{3}$ [3]. Puiggalí et al. later suggested that the β-form rests on a frustrated packing of three 3_1 helix chains in a trigonal unit cell with parameters $a = b = 1.052$ nm, $c = 0.880$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, with a space group $P3_2$ [5]. This frustrated structure seems to be formed to accommodate the random up-down orientation of neighbor chains associated with the rapid crystallization under stretching [5].

The γ form is obtained via epitaxial crystallization on hexamethylbenzene substrate. It is characterized by two antiparallel helices with 3_1 conformation packed in an orthorhombic unit cell with $a = 0.995$ nm, $b = 0.625$ nm, $c = 0.880$ nm [6]. The a (0.892 nm) and b (0.886 nm) axes of hexamethylbenzene crystals are close to the chain axis repeat distance of the γ form of PLLA in the 3_1 helical conformation (0.880 nm). This matching favors the epitaxial growth of γ form crystals of PLLA on hexamethylbenzene crystal surface.

Besides these three main crystal polymorphs, a disordered modification of the α form, named α′ form, was recently proposed for PLLA. The WAXD patterns of the α and α′ forms of PLLA are very similar, with small differences seen in the shift to higher 2θ values of the two strongest reflections, assigned to the (1 1 0)/(2 0 0) and (2 0 3) planes, and in the appearance of a weak reflection at $2\theta = \approx 24.5^\circ$ in the α′ modification. This corresponds to a similar packing of the two polymorphs, as, analogous to the α form, the PLLA chains in the α′ modification have a 10_3 helix conformation and orthorhombic (or pseudo-orthorhombic) unit cell [7–9]. The

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lattice spacings for the (1 1 0)/(2 0 0) and (2 0 3) planes of α' form crystals are somewhat larger than those of their α counterparts, indicating that the α' form has slightly larger lattice dimensions [7,10]. Upon melt or cold crystallization conditions, the α' form is known to grow at low temperatures, whereas crystallization at high temperatures leads to formation of the α modification. The exact temperature range where each of the two polymorphs prevails depends on the specific PLLA grade. Upon heating, the less stable α' crystals transform to the α form, which results in the appearance of multiple endotherms and possible exotherms when PLLA is analyzed by calorimetry [8–10].

Crystal polymorphism is known to have a large influence on thermal properties of semicrystalline polymers. The variation in melting behavior caused by different thermal stability of the crystal modifications, and the possible interconversion among the various crystal forms, as reported for PLLA, are the most commonly analyzed effects. In some cases, a variation in the crystal modification may affect not only the crystal phase, but also the thermal properties of the amorphous segments. This is the case, for instance, of isotactic poly(1-butene) (PB-1), as the spontaneous transformation of the metastable form II to the more stable form I results in a slight increase of the glass transition temperature and in a large increase of the rigid–amorphous to mobile–amorphous ratio, despite an unchanged crystallinity [11]. These effects are due not only to a shrink of the crystals associated to the solid–solid phase transformation, caused by a much higher density of form I packing, but also to the different mobility of PB-1 chains within the crystals, as the large-amplitude intramolecular chain motion of the tetragonal form II makes it a conformational disordered (condis) crystal [12].

Some varied degree of order of the different crystal polymorphs was also proposed for poly(L-lactic acid): the molecular packing within the unit cell of α' form PLLA is looser and disordered, with larger lattice dimension and weaker interchain interaction [7,9,10]. A preliminary analysis by Zhang et al. [13] suggested that the chain conformation of α and α' crystal modifications are somewhat different, but quantitative results have not been reported yet. The disorder of the chains within the α' crystals is conformational, which makes this crystal modification a mesophase (condis crystal) [14]. As discussed in this contribution, the varied disorder of the crystal packing in PLLA affects the thermal properties not only of the crystal phase, but also of the coupled amorphous portions. Two types of amorphous fractions are usually present in semicrystalline polymers: a mobile amorphous phase (MAF), made of the polymer chains that mobilize at the glass transition temperature (T_g), and a rigid amorphous fraction (RAF), made of the polymer chains coupled with the crystal phase that usually devitrify at higher temperatures [15,16]. The influence of crystal polymorphism on the relative ratio of the crystal and of the two amorphous fractions is also analyzed in this contribution. As the thermal properties of poly(lactic acid) are highly affected by the stereochemistry of the repeating unit [17], a polymer with a very high amount of L-lactic acid was used.

2. Experimental

2.1. Materials and sample preparation

Poly(L-lactic acid) (PLLA), Biomer L9000, was purchased from Biomer Biopolyesters, Germany. Before use PLLA was dried in a vacuum oven at 60 °C for 24 h to avoid hydrolysis of the polymer during melt-processing.

After drying, the PLLA chips were compression-molded with a Carver Laboratory Press at a temperature of 185 °C for 4 min, without any applied pressure, to allow complete melting. After this period, a pressure of 150 bar was applied for 2 min. Successively the press plates, equipped with cooling coils, were quickly cooled to room temperature by cold water.

The as-prepared PLLA films were crystallized in oven at different crystallization temperatures (T_c = 85, 95, 105, 115, 125, 145, 165 °C) for 18 h. At low T_c (85 °C) the crystallization time was extended to 66 h because of the slow crystallization rate, as discussed below.

2.2. Wide angle X-ray analysis

The crystalline structure of PLLA crystallized at different T_c was investigated by wide-angle X-ray diffraction analysis (WAXS). WAXS investigations were carried on PLLA films by means of a Philips (PW 1050 model) powder diffractometer (Ni-filtered CuKα radiation) equipped with a rotative sample holder. The high voltage was 40 kV and the tube current was 30 mA.

The degree of crystallinity (w_C) of PLLA films was evaluated according to the Hermans–Weidinger method, as w_C is given by the ratio between the diffraction due to the crystalline phase (I_c) and the total diffraction intensity arising from both the amorphous (I_a) and crystal parts [18]:

$$w_C = \frac{I_c}{I_c + I_a} \tag{1}$$

The crystallinity values shown below are averaged from seven different PLLA films for each T_c.

2.3. Calorimetry

The thermal properties of PLLA films were measured with a Perkin–Elmer Pyris Diamond DSC, equipped with Intracooler II as cooling system and with a Mettler DSC 822^e calorimeter equipped with a liquid-nitrogen cooling accessory. Both the instruments were calibrated in temperature with high purity standards (indium and cyclohexane) and in energy with heat of fusion of indium. Dry nitrogen was used as purge gas at a rate of 48 ml/min. To obtain precise heat capacity data, each measurement was accompanied by an empty pan run, and a calibration run with sapphire under identical conditions [19]. All the measurements were repeated at least three times to improve accuracy.

The conventional differential scanning calorimetry (St-DSC) analyses were conducted with the Perkin–Elmer Pyris Diamond DSC at the scanning rate of 20 °C/min. Temperature-modulated calorimetry (TMDSC) at the underlying heating rate of 2 °C was conducted with the Perkin–Elmer Pyris Diamond DSC using a modulation amplitude of 0.4 °C and periods of temperature oscillations ranging from 60 to 120 s. Quasi-isothermal TMDSC data were gained with the Mettler DSC 822^e calorimeter, using a sawtooth oscillation with a temperature amplitude of 0.4 °C and a modulation period of 60 s about a base temperature T_o, which was raised stepwise in temperature increments of 5 °C after 16 min at each T_o.

From TMDSC measurements the reversing specific heat capacity was obtained from the ratio of the amplitudes of modulated heat flow rate and temperature, both approximated with Fourier series [20,21]. The reversing specific heat capacity values reported in this contribution were obtained from the first harmonics of the Fourier series. Similar to conventional DSC analyses, each TMDSC measurement was accompanied by an empty pan run, and a calibration run with sapphire under identical conditions [19]. The good agreement between the experimental data and the thermodynamic heat capacity of solid and liquid PLLA [22] proves that the modulation periods used are long enough to be corrected satisfactorily by the calibration with sapphire.