Polymer Degradation and Stability 108 (2014) 140–150

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Crystallization and thermal characterization of biodegradable tri-block copolymers and poly(ester-urethane)s based on PCL and PLLA

Iván Navarro-Baena [a], José M. Kenny [a,b], Laura Peponi [b,*]

[a] Dipartimento di Ingegneria Civile e Ambientale, Università di Perugia, Italy
[b] Instituto de Ciencia y Tecnología de Polímeros, ICTP-C.S.I.C., Spain

ARTICLE INFO

Article history:
Received 8 December 2013
Received in revised form
11 February 2014
Accepted 11 March 2014
Available online 20 March 2014

Keywords:
Poly(L-lactic acid)
Poly(ε-caprolactone)
Poly(ester-urethane)
Isothermal crystallization
WAXD
Thermogravimetric analysis

ABSTRACT

In this paper the crystallization behavior of biodegradable linear tri-block copolymers PLLA-b-PCL-b-PLLA and their corresponding poly(ester-urethane)s was studied and related to their thermal stability. A series of tri-block copolymers was synthesized by ring opening polymerization of L-lactic acid thus using PCL block with constant molecular weight of about 8000 g/mol and varying the amount of PLLA. The poly(ester-urethane)s were synthesized by polycondensation of the tri-block copolymers with hexamehylene diisocyanate. The crystallinity nature of the polymers was investigated by wide angle X-ray diffraction (WAXD) measurements allowing the determination of the cell structure parameters. Furthermore, the kinetic of the crystallization process from the melt was studied with differential scanning calorimetry (DSC) measurements and by using the Avrami equation to describe the process in terms of crystallization growth and rate. Finally, the thermal degradation of the tri-block copolymers as well as of the poly(ester-urethane)s was investigated by dynamic thermogravimetric analysis (TGA). It was found that the differences on the molecular structure in terms of block copolymer composition, molecular weight, crystallinity and the presence of urethane bonds, affect the degradation behavior of each block.

1. Introduction

The interest on aliphatic polyesters for the design of new materials for biomedical applications has increased in recent years [1,2]. Among them, poly(L-lactic-acid) (PLLA) and poly(ε-caprolactone) (PCL) have been widely studied due to their interesting biodegradable as well as biocompatible properties. Actually these polymers show different mechanical and thermal behavior; for instance, PLLA is a brittle polymer with a glass transition temperature (T_g) around 60 °C and a melting temperature (T_m) about 160 °C, while PCL is a rubbery polymer with T_g around −60 °C and the T_m close to 50 °C. Furthermore the combination of these polymers, such as through copolymerization or blending, has been studied by several researchers in order to design new multifunctional materials with unique properties [3,4]. Depending on their molecular weight these polymers can crystallize and so it is possible to design their synthesis tailoring their thermal properties [4–6].

The analysis of the crystallization process of semi-crystalline polymers can lead to a better understanding of their thermal behavior as well as of their final properties [7–11]. Moreover, for the copolymers composed by crystalline segments, these studies become very useful and interesting to understand the effect of each monomer on the crystallization behavior of the other one [5,12–14]. The Avrami theory for the isothermal crystallization of polymers [15] involves the study of the crystallization growth and rate and it can be used for homopolymers [8], blends [16] as well as for copolymers [17]. Also the energy of activation for the crystallization process can be determined from the isothermal crystallization results [18,19]. In particular, the crystallization of PLLA and PCL has been studied by many research groups. PCL crystallizes in a primitive orthorhombic cell having two polymer chains with opposite orientation into the unit cell and the space group is $P2_12_12_1$ [20]. On the other hand, PLLA can crystallize showing different polymorphisms, namely the alpha, beta and gamma forms. Usually, from the solution or the melt, PLLA crystallizes in the alpha form, while beta and gamma forms are obtained only through specific

* Corresponding author. C/Juan de la Cierva, 3, 28066 Madrid, Spain. Tel.: +34 912587424; fax: +34 915644853.
E-mail address: lpeponi@ictp.csic.es (L. Peponi).

http://dx.doi.org/10.1016/j.polymdegradstab.2014.03.012
0141-3910/

treatments [9,21,22]. De Santis and Kovacs reported the PLLA alpha crystallization form for the first time [23] and since then, many other reports can be found in the scientific literature on the same subject [11,24,25]. Moreover, another crystalline form called alpha prime, described as a disordered form of the alpha form, has been found to occur in high undercooling crystallizations [26].

The thermal degradation of polyesters has been object of extensive studies. In particular, this kind of polymers shows two degradation processes, the random chain scission and the specific chain end scission [27]. Specifically, the effects of thermal degradation in copolymers of PCL and PLLA have been studied in the last years [28–30]. So, PCL degrades at higher temperatures than PLLA and these temperatures strongly depend on the molecular weight of the polymers. Also it is important to remark that the presence of residual catalyst can induce the depolymerization of the polyesters at lower temperatures [31].

In this work, different linear tri-block copolymers based on PCL and PLLA, PCL-b-PLLA-b-PCL, have been polycondensed with isocyanates in order to produce poly(ester-urethane)s varying both the molecular weight of PLLA and the ratio between the PCL and PLLA blocks. Then, both tri-block copolymers and poly(ester-urethane)s have been studied in terms of stability and degradation, correlating their degradation behavior with their crystalline nature. In particular, the crystalline structure of the copolymers has been studied by using the WAXD analysis as well as by applying the Avrami equation. WAXD has been used in order to obtain the main parameters for the unit cell and the crystal size, while the crystallization process from the melt has been studied by DSC isothermal measurements focusing the attention on the crystallization process in terms of crystallization rate and growth. So, the effects provoked in the crystallization process due to the presence and the nature of each co-monomer in the final copolymers are specifically discussed. A deep study on the crystallization behavior is necessary for the design of stimuli responsive materials such as shape memory polymers considering that the crystallinity phase can act as transient phase. In this case, due to their double crystalline nature, the poly(ester-urethane)s studied show shape memory behavior at different deformations such as 50, 100, 200 and 350% as reported elsewhere [3]. Consequently, this study is concentrated on the crystallization behavior of materials designed to show shape memory behavior. Finally, the effects of the chemical composition on the thermal degradation are investigated by means of thermogravimetric analysis (TGA) focusing the attention on the different stability behavior of both the initial tri-block copolymers and the poly(ester-urethane)s due to their different chemical and crystalline structure.

2. Materials and methods

2.1. Synthesis of the materials

The tri-block copolymers were synthesized by ring opening polymerization of L-lactide using the hydroxyl end groups of PCL-diol as initiator. The reaction was performed in bulk, L-lactide and PCL-diol was mixed in a round bottom flask using 0.1% wt of $Sn(Oct)_2$ as catalyst. The mixture was heated at 180 °C for 3 h under stirring. When the reaction was finished the product was dissolved in chloroform and precipitated in cold methanol. The final product was filtered off and dried for 24 h at room temperature with a high vacuum pump. In our previous work the same synthesis procedure was employed to obtain di-block copolymers of PCL-b-PLLA [3].

The poly(ester-urethane)s (PUs) were synthesized dissolving the tri-block copolymers and the HDI in dichloroethane in a round bottom flask and using 0.1% wt of $Sn(Oct)_2$ as catalyst. The reaction was carried out at 80 °C during 5 h. The product was casted in a Petri dish for solvent evaporation. The films obtained were dried for 24 h at room temperature under vacuum in order to ensure the removal of the solvent.

L-Lactide (L-LA), ε-caprolactone (ε-CL), hexamethylene diisocyanate (HDI) and the catalyst tin(II) 2-ethylhexanoate (Sn(Oct)2) were purchased by Sigma Aldrich. The PCL-diol CAPA 2803 was kindly donated by Perstorp. All the materials were employed without further purification.

2.2. Nuclear magnetic resonance

The chemical structure was investigated by means of proton Nuclear Magnetic Resonance (^{1}H NMR) with a Varian Mercury Plus NMR 400 MHz apparatus. 10 mg of sample were dissolved in deuterated chloroform. The solution was filtered off with a cotton filter before the analysis. The spectra were recorded by the accumulation of 32 spectra. The molecular structure of the tri-block copolymers were studied taking into account the work of Kasperczyk et al. [32].

2.3. Morphological characterization

The morphology of the poly(ester-urethane)s was analyzed by Field Emission Scanning Electron Microscopy (FE-SEM Supra 25, Zeiss). The polymer samples were cut by using liquid N2, and the transversal area has been analyzed. All the samples were gold coated by an Agar automatic sputter coated.

Atomic Force Microscopy (AFM) analysis was performed operating in tapping mode (TM) with a scanning probe microscope (NanoScope IV, Digital Instruments Multimode TM, from Veeco). Height and phase images were obtained under ambient conditions with typical scan speed of 0.5–1 line/s, using a scan head with a maximum range of 16 μm × 16 μm. Only the TM-AFM phase image is reported in this research.

2.4. Wide-angle X-ray diffraction analysis

Wide-Angle X-ray Diffraction (WAXD) measurements were performed using a Bruker D8 Advance instrument with a Cu Kα source (0.154 nm) and a Detector Vantec1. The scanning range was 2°–50°, step-size and count time per step were 0.023851° and 0.5 s, respectively. The interplanar distance (d_{hkl}) was calculated through the application of the Bragg equation considering that it is well known that, in the case of PCL and PLLA, both polymers crystallize in the orthorhombic crystal system [23,24].

Furthermore, from the WAXD data, also the crystal size in the (*hkl*) direction can be obtained through the Scherrer equation (Eq. (1)).

$$D = \frac{k\lambda}{\beta cos(\theta)} \quad (1)$$

In the Eq. (1), D is the crystal size, k is the shape factor with a typical value of 0.9 [33], λ is the wavelength of the incident wave, β is the broadening of the peak at half of the maximum peak and θ is the diffraction angle.

2.5. Isothermal crystallization analysis

The isothermal DSC measurements were performed in a Perkin Elmer DSC 8500 instrument. The working temperatures have been chosen taking into account the dynamic DSC experiments. The experimental data of the isothermal crystallization from the melt can be fitted by the expression of the Avrami equation (Eq. (2)) [34,35].