Polymer 67 (2015) 227–239

Contents lists available at ScienceDirect

Polymer

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

Homocrystal and stereocomplex formation behavior of polylactides with different branched structures

Sahar Nouri, Charles Dubois*, Pierre G. Lafleur

CREPEC, Chemical Engineering Department, Ecole Polytechnique, C.P. 6079, Succ. Centre Ville, Montreal, QC H3C 3A7, Canada

ARTICLE INFO

Article history:
Received 21 January 2015
Received in revised form
10 April 2015
Accepted 21 April 2015
Available online 28 April 2015

Keywords:
Branched polylactide
Crystallization
Stereocomplex

ABSTRACT

Effect of chain architecture on homocrystallization and stereocomplex formation behavior of polylactide (PLA) in quiescent conditions was investigated by means of differential scanning calorimetry (DSC) and optical microscopy. Non-isothermal and isothermal crystallization of star shaped, comb like and hyper branched poly(L-lactides) (PLLAs) with similar molecular weights were studied and compared to a linear one. In dynamic mode, branched PLAs reached higher crystallinity and revealed much higher spherulite density as compared to linear PLA. Also blends of linear and branched PLA with different blending ratios revealed faster crystallization than neat linear PLA. Based on kinetics data obtained in isothermal crystallization experiments, much faster crystallization was achieved with a 4–14 fold decrease in crystallization half-time as a consequence of non-linear chain architecture. Crystallization upon cooling, reduced cold crystallization temperature, increased spherulite density and lower Avrami exponent values for branched PLAs in comparison to linear one suggest enhanced nucleation process as a result of a branched chain architecture. On the other hand, total crystallinity and growth rate were decreased by branching. Stereocomplex formation between linear PLLA and branched poly(D-lactides) (PDLAs) showed dependency of stereocomplex formation to branched architecture. Also, stereocomplex crystals nucleated PLA homocrystallization process while different internal morphology between stereocomplex and homocrystal spherulites was observed. These results confirm that chain architecture has a profound effect on the crystallization behavior of PLA.

1. Introduction

Application of bio-based polymers has surged throughout the past decade due to their reduced environmental impact as compared to traditional polymers. Polylactide (PLA) is a leading member of this family of polymers which has been in the spotlight; having the edge over competitive bioplastics because of its degradability and acceptable mechanical, optical and barrier properties. Existence of lactic acid in two stereo-isomer forms known as L and D results in a wide variety of PLA grades from the crystallization point of view. PLA can be completely amorphous or semi-crystalline with different melting temperatures and crystallinity depending on the amount and placement of L and D units in polymer chain [1–5]. Also, different crystal types have been identified for PLA, the most frequently occurring is α type crystal with a pseudo-orthorhombic cell structure with cell dimensions of $a = 1.07$ nm, $b = 0.595$ nm, and $c = 2.78$ nm, containing two 10_3 helices [6]. For stereochemically pure PLAs with high enough molecular weights, melting temperature could be as high as 180 °C [3,5]. Another PLA crystal type is known as stereocomplex crystal and was first reported by Ikada et al. [7]. Although opposite repeating units in PLA chain can hinder its crystallization, when PLLA and PDLA chains are mixed, they can co-crystallize and form stereocomplex. Stereocomplex cell structure is triclinic with dimensions of $a = 0.916$ nm, $b = 0.916$ nm and $c = 0.870$ nm, in each cell one PLLA and one PDLA chain segment are located assuming a 3_1 helical conformation [6]. The crystal formed from the co-crystallization of PLLA and PDLA melts at about 50 °C higher than homopolymer crystals.

It is well established that crystallinity is a major parameter in determining several polymer properties. In the case of PLA, slow crystallization and low crystallinity are among its main weaknesses [8]. Usually PLA does not crystallize completely from the melt and

---

* Corresponding author.
E-mail addresses: charles.dubois@polymtl.ca, charles_dubois@me.com (C. Dubois).

http://dx.doi.org/10.1016/j.polymer.2015.04.065

shows cold crystallization behavior upon subsequent heating [9,10]. This can be used to increase the crystallinity of final product. Other methods such as adding nucleating agents [2,11–14], plasticizers [15–17] or their combination [18,19] may also be used for increasing the number of crystallization sites and chain mobility; therefore, enhancing the overall crystallization kinetics of PLA.

Another type of modification is changing chain architecture from linear to a branched one. Different methods have been used to produce branched PLA such as free radical branching [20–22], using chain extenders [23–27], multifunctional initiators [28–30] or the combination of synthesis and chain extension methods [31], as well as copolymerization with other monomers [32,33]. Although these studies revealed the effect of branching on changing PLA properties, their focus was mainly on melt rheology. Crystallization of branched PLA is explored to a smaller extent in comparison to linear PLA; especially for stereocomplex crystal. In addition, results are inconsistent from different aspects. There are some reports that branching increased the crystallization rate [26,34,35] while other reports exist on slower crystallization by increased number of branches [29,36]. In addition, while some researchers presented a reduction in melting temperature by less perfect crystals [31,37], others showed that T_m was not affected by chain branching [29,38]. Also by increasing branch content, crystallinity (X_c) is reported to decrease or remain unaffected [38–40]. Furthermore, most of the published data are on PLAs randomly branched through reactive processes that can influence their molecular weight. Therefore, the pure effect of chain architecture in well defined structures is less examined. In this work, we focused on this aspect by a comprehensive study of branched PLA crystallization kinetics and morphology. Homocrystallization of three branched chain architectures, i.e. star shaped, comb like and hyper branched PLA was compared with linear PLA as well as stereocomplex formation between linear PLLA and branched PDLAs. Interesting results were obtained on crystalline morphology and improvement of crystallization behavior for both crystal types.

2. Experimental

2.1. Materials

PLLA and PDLA with different branched architectures were synthesized by ring-opening polymerization of L-lactide and D-lactide (Purac Biochem, The Netherlands), respectively. Reaction was conducted at 180 °C for 1 h under the nitrogen atmosphere. Tin(II) 2-ethylhexanoate (Aldrich) was used as the catalyst at a concentration of 0.03 mol%. Pentaerythritol and Triglycerol (Sigma–Aldrich) were used as initiator to prepare star shaped and comb like polymers, while Glycidol (Sigma–Aldrich) was used as initiator-comonomer to produce hyper branched structure. Molecular weight and its distribution was obtained using a Viscotek GPCmax equipped with light scattering detector. To confirm the structure of synthesized materials, ^{1}H NMR characterization was performed by a Bruker AV500 spectrometer. M_n and PDI of star shaped PLA were equal to 89 kg/mol and 1.38, respectively. Base on the NMR data, absence of non-reacted hydroxyl groups of the initiator indicated that four-arm star structure was successfully synthesized. Therefore, the average arm molecular weight was 22.25 kg/mol. M_n and PDI of comb like PLA were equal to 85 kg/mol and 1.74, respectively. According to NMR analysis, 94.6% of hydroxyl groups were reacted. Thus, average backbone and arm molecular weights were 36.2 and 17.9 kg/mol. For hyper branched structure, M_n of 89 kg/mol and PDI of 1.39 were obtained. Although it was not possible to quantify the branch density because of the complex structure of this polymer, formation of randomly branched structure was verified from NMR characterization. More details regarding the synthesis and structure characterization including NMR spectra can be found in a previous paper by this group [41]. In addition, a commercial linear PLLA (4032D from NatureWorks) with a molecular weight of 101 kg/mol was used in this study as a reference and for blending purpose. Polymers are identified with two letters; X–Y. The first letter (X) indicates the stereochemistry of PLA, L for PLLA and D for PDLA. The second letter (Y) represents the chain structure, L for linear, S for star shaped, C for comb like and H for hyper branched PLA. For example, D-H means PDLA with hyper branched structure.

2.2. Blending

To study the effect of synthesized polymers on the crystallization behavior of commercial PLA, different blends were prepared by melt blending. Prior to the process, polymers were dried at 80 °C for 12 h. A Leistritz ZSE 18 mm co-rotating twin-screw extruder operating at 190 °C and a rotation speed of 100 rpm was used to prepare the blends.

2.3. Characterizations

Differential scanning calorimetry by TA instrument DSC Q1000 was performed to study the isothermal and non-isothermal crystallization behavior as well as melting of the specimens. In dynamic mode, after removing thermal history at 200 °C for homocrystal or 240 °C for stereocomplex, samples were cooled to 20 °C and then heated again at a rate of 10 °C/min. For isothermal mode, after removing thermal history, samples were rapidly cooled to crystallization temperature and enough time was given to complete the crystallization process. Hot-stage optical microscopy observations were conducted to evaluate crystalline morphology (spherulite size and density) and spherulite growth rate. OPTIPHOT-2 optical microscope equipped with a programmable hot stage (Mettler FP82HT) was employed using similar thermal procedures as in DSC tests. Samples were in the form of thin films, prepared by hot pressing technique.

3. Results and discussion

3.1. Homocrystallization

In the first step, PLLA homocrystallization (absence of PDLA chains) in non-isothermal and isothermal modes at quiescent conditions was studied from different aspects, including kinetics, crystallinity and morphology.

3.1.1. Non-isothermal crystallization

Crystallization of linear, star shaped, comb like and hyper branched PLLAs in non-isothermal conditions were compared through DSC characterizations. Thermal history of the specimens was removed by melting at 200 °C for 3 min. Temperature was then reduced to 20 °C at a rate of 10 °C/min to record the crystallization behavior upon cooling the melt. Finally, temperature was increased at the same rate to 200 °C to observe thermal response in a subsequent heating cycle. Fig. 1 shows DSC thermograms where heat flow data obtained by applying this procedure were plotted versus temperature. Cooling and heating cycles are shown in Fig. 1 left and right, respectively. Linear PLA did not reveal a crystallization peak in cooling which is expected from the very slow crystallization kinetics of PLA. Also, in the heating cycle, only a slight cold crystallization was observed at 140 °C followed by a small melting peak at 170 °C. Branched PLAs on the other hand showed a completely different crystallization behavior. In cooling mode, all three branched structures showed a crystallization peak at about 102 °C.