University of Naples Federico II



# Interplay between crystals and bubbles in PLLA

## Alessandra Longo

PhD in Industrial Product and Process Engineering - XXXIV cycle Department of Chemical, Materials and Production Engineering

> Tutor: Prof. E. Di Maio Cotutor: Dr. M.L. Di Lorenzo

Academic Year 2021-2022

### Contents

Abstract	1
Chapter 1 - Introduction	3
1.1 The Importance Of Biodegradable Plastics	3
1.2 Poly (L-Lactic Acid)	7
1.3 Poly(L-Lactic Acid) Foaming	12
1.3 Aim Of The Work	17
1.4 References	18
Chapter 2 - Enhancement of crystallization kinetics of poly(L-lactic acid	) by grafting
with optically pure branches	29
2.1 Introduction	29
2.2 Materials And Methods	31
2.3 Results And Discussion	36
2.3 Conclusions	49
2.4 References	51
Chapter 3 - Heterogeneous bubble nucleation by homogeneous crystal n	uclei in poly
(L-lactic acid) foaming	55
3.1 Introduction	55
3.2 Materials And Methods	58
3.2 Materials And Methods 3.3 Results And Discussion	58 62
<ul><li>3.2 Materials And Methods</li><li>3.3 Results And Discussion</li><li>3.4 Conclusions</li></ul>	58 62 70
<ul><li>3.2 Materials And Methods</li><li>3.3 Results And Discussion</li><li>3.4 Conclusions</li><li>3.6 References</li></ul>	58 62 70 71
<ul> <li>3.2 Materials And Methods</li> <li>3.3 Results And Discussion</li> <li>3.4 Conclusions</li> <li>3.6 References</li> </ul> Chapter 4 - CO <sub>2</sub> -induced mesophase: an easy and green method to tailor creations	58 62 70 71 <b>rystallization</b>
<ul> <li>3.2 Materials And Methods</li> <li>3.3 Results And Discussion</li> <li>3.4 Conclusions</li> <li>3.6 References</li> <li>Chapter 4 - CO<sub>2</sub>-induced mesophase: an easy and green method to tailor creating kinetics and morphology in PLLA</li> </ul>	58 62 70 71 rystallization 77
<ul> <li>3.2 Materials And Methods</li> <li>3.3 Results And Discussion</li> <li>3.4 Conclusions</li> <li>3.6 References</li> <li>Chapter 4 - CO<sub>2</sub>-induced mesophase: an easy and green method to tailor creating the second secon</li></ul>	58 62 70 71 <b>rystallization</b> 77 77
<ul> <li>3.2 Materials And Methods</li> <li>3.3 Results And Discussion</li> <li>3.4 Conclusions</li> <li>3.6 References</li> <li>Chapter 4 - CO<sub>2</sub>-induced mesophase: an easy and green method to tailor creating the second secon</li></ul>	58 62 70 71 <b>rystallization</b> 77 77 80
<ul> <li>3.2 Materials And Methods</li> <li>3.3 Results And Discussion</li> <li>3.4 Conclusions</li> <li>3.6 References</li> <li>Chapter 4 - CO<sub>2</sub>-induced mesophase: an easy and green method to tailor creating the second secon</li></ul>	58 62 70 71 <b>rystallization</b> 77 77 80 81
<ul> <li>3.2 Materials And Methods</li> <li>3.3 Results And Discussion</li> <li>3.4 Conclusions</li> <li>3.6 References</li> <li>Chapter 4 - CO<sub>2</sub>-induced mesophase: an easy and green method to tailor creating the second secon</li></ul>	58 62 70 71 <b>rystallization</b> 77 77 80 81 89
<ul> <li>3.2 Materials And Methods</li> <li>3.3 Results And Discussion</li> <li>3.4 Conclusions</li> <li>3.6 References</li> <li>Chapter 4 - CO<sub>2</sub>-induced mesophase: an easy and green method to tailor cukinetics and morphology in PLLA</li> <li>4.1 Introduction</li> <li>4.2 Materials And Methods</li> <li>4.3 Results And Discussions</li> <li>4.3 Conclusions</li> <li>4.4 Supporting Information</li> </ul>	58 62 70 71 <b>rystallization</b> 77 77 80 81 89 90
<ul> <li>3.2 Materials And Methods</li> <li>3.3 Results And Discussion</li> <li>3.4 Conclusions</li> <li>3.6 References</li> <li>Chapter 4 - CO<sub>2</sub>-induced mesophase: an easy and green method to tailor creating the second secon</li></ul>	58 62 70 71 <b>rystallization</b> 77 77 80 81 89 90 94

## Abstract

The present thesis focuses on the study of the relationship between the thermal properties of poly (L-lactic acid) (PLLA) and its foaming behavior.

PLLA is the most extensively studied and used biodegradable and renewable thermoplastic polyester, due to its potential to replace conventional petrochemical-based polymers. It is biocompatible, derived from annually renewable resources, and is used in a variety of industrial fields, which include films for packaging or agriculture, biomedicine, or for production of foams. Besides being used for tissue engineering and medical implants, PLLA foams have several additional applications such as thermal and sound insulation in construction and food packaging industry.

PLLA has also few shortcomings. One of the most serious is its low crystallization kinetics, which limits a wider industrial application of this biopolymer. Common procedure to overcome this drawback includes blending with plasticizers or addition of nucleating agents. Moreover, the great variety of PLLA foams applications depends on the foam structure in terms of their density and morphology, both in the dimension and the distribution of cells within the material. The addition of external nucleating agents has been proposed also in this case, as a solution to tune foam morphology. But, despite the positive effects of the heterogeneous nucleation both of crystals and bubbles conveyed by nucleating agents, compounding with different polymers or the inclusion of particles of a different material can make the biodegradation process harder and may alter the biocompatibility of the polymer.

Thus, in this thesis, three methodologies to tune both thermal properties and foam morphology preserving the purity and homogeneity of the material, i.e., without the addition of external agents, are presented.

In order to enhance crystallization rate of PLLA, a structural modification of the polymer chain, by addition of side chains of the same chemistry, has been attempted. The aim is to obtain a branched structure where fast-crystallizing short branches can favor overall crystallization. A PLLA branched copolymer, where branches are made of optically pure PLLA, has been synthetized. Its crystallization kinetic is much higher than both the starting commercial PLLA grade, and a blend having the same nominal composition.

Partial crystallization of the polymer before or during foaming represents a key issue in foaming technology. Polymer crystals are well known to behave as heterogeneous nucleation sites for bubble formation, enhancing cell nucleation during foaming. However, at the same time, large degrees of crystallization increase stiffness of the polymer, resulting in a depression of the expansion

ratio. However, fine tuning of crystallization may favor design foam morphology. An ideal situation, which implies a high number of very small crystals with the lowest possible crystal fraction has been studied in this thesis, by controlled development of nano-sized ordered chain aggregates, known as homogeneous crystal nuclei, before foaming.

Annealing glassy PLLA in the glass transition temperature range allows formation of homogeneous crystal nuclei, which enhance/accelerate subsequent crystallization upon raising the temperatures by reducing the energy barrier needed to create new surfaces. The large advantage of homogeneous nuclei, compared to existing crystals, is the absence of initial crystallinity which, coupled to their very high density per unit volume, should provide an enormous number of sites for bubble growth.

Experiments of foaming glassy PLLA annealed for various times have been conducted. Results showed that proper choice of nucleation time and nuclei density have favorable and desired effects on foam morphology. Hence it is demonstrated, for the first time, that homogeneous crystal nuclei can successfully promote not only the known crystal nucleation, but also nucleation of bubbles, thus allowing to increase expansion ratio and tune foam morphology.

It needs to be underlined that such studies require precise temperature/pressure control during experiments, not attainable with the available instrumentation, since variation of internal pressure cause sizable change of the temperature of the pressure vessel. Therefore, part of the research work has been devoted to design and construction of a novel pressure vessel, where temperature fluctuations upon variation of internal pressure are minimized.

With the gained knowledge on interplay between crystals and gas in PLLA foaming, the final part of the research has been dedicated to the effect of  $CO_2$  on chain reorganization of the polymer. At low temperature (around room temperature),  $CO_2$  can induce formation of a metastable mesophase, named  $\alpha$ "-form that, upon further heating, transforms to stable  $\alpha$ -crystals.

Both melt-quenched and annealed PLLA were exposed to low CO<sub>2</sub> pressures at room temperature for short period of time not exceeding 20 minutes to induce mesophase formation, which is known to increase with saturation time. The kinetics of formation CO<sub>2</sub>-induced mesophase was studied in a PLLA containing homogeneous crystal nuclei, then non-isothermal crystallization of PLLA containing both homogeneous crystal nuclei and mesophase has been investigated. It all lead to a deeper knowledge on how thermal treatment and CO<sub>2</sub> conditioning represent fast, green and cost-effective ways to tune crystallization kinetics of PLLA.

## **Chapter 1**

## Introduction

### 1.1 The importance of biodegradable plastics

The history of synthetic polymers has its roots in the early 20th century. In 1907, the first synthetic plastic was produced by the Belgian chemist Leo Baekeland in New York, by mixing phenol and formaldehyde in the presence of a catalyst. Heating this mixture under pressure, he obtained a thermosetting polymer. In a few years the material, named "Bakelite" after him, became a commercial success finding application mainly in electrical insulation.

In 1945, Yarsley and Couzens published a book named "Plastics" praising it as the most promising material with almost inexhaustible possible applications [1]. In the final chapter of their book, they predict what they called plastic age with the figure of a plastic man whose life is surrounded by plastic in any field and in any age of its life, from his birth, with toys and teething rings, to his death, with coffin made of plastic.

The huge growth of industrial production of plastics started soon later, in the mid 1950s, thanks to the world-famous Ziegler-Natta catalyzers [2], developed during the collaboration of Karl Ziegler and Giulio Natta, and peaked with the synthesis in 1954 of isotactic polypropylene, which paved the way to production of stereospecific polymers patented as Moplen.

After this milestone, the production of plastics has continuously increased since 1950 at an average of 8.7% per year, growing from 1.7 million tons to approximately 370 million tons in 2019 [3], confirming the prediction made by Yarsley & Couzens in 1945.

This massive production of plastics is mainly due to their versatility of properties, which widen the range of applications. The advent of plastics brought remarkable benefits and its characteristics of lightweight, easiness in production and processing, high thermal and electrical insulation, chemical and corrosion resistance and shatterproof, make plastic the ideal substitute to different materials such as glass or metal in many applications for daily life. The revolution of plastics

influenced all aspects of human life, from transports, helping in increasing the lightness of vehicles, to food packaging, allowing to control storage atmosphere and preservation of goods [4]. People embraced the advent of plastic and disposable products. Emblematic is the photograph published on a 1955 number of LIFE magazine in an article entitled "Throwaway Living" (Figure 1.1), where a family celebrates the dawn of single-use products that cut down on household chores.



Figure 1.1. Throwaway Living, article published on LIFE magazine in 1955

Plastics represent not only an improvement in life quality of billions of people, but the plastic industry is also fundamental for Europe's economy. All the industrial sectors involving plastics, from the raw producers to third use manufacturers and recyclers, employ over 1.5 million people in Europe, through more than 55000 companies, with a contribution on European public finances which in 2019 reached more than 30 billion euros [3].

According to Plastics Europe Market Research Group (PEMRG) and Conversio Market & Strategy GmbH, in 2019 global plastics production almost reached 370 million tons with almost 58 million tons produced in Europe. The biggest end-use markets are represented primarily by packaging, with the almost 40% of plastic converters demand and building and construction with a demand of 20% on a total European demand of 51 million tons. This is summarized in Figure 1.2, which reports European plastic demand distribution by resin type, estimated in 2019 [3].



Figure 1.2. European plastics demand distribution by polymer types in 2019 (source: Plastic Europe 2020)

As evidenced in Figure 1.2, most plastic materials are fossil-based, and in Europe about 4-6% of the overall consume of oil and gas is related to plastic production. Despite the benefits enjoyed from the advent of "plastic era", the massive use of plastics brought together with innovative solutions also fundamental drawbacks affecting the environment.

Together with the rapid consumption of non-renewable resources, waste disposal of postconsumer plastics represents an important issue. There are three possibilities for the end-of-life plastic management: energy recovery, recycling and disposal in landfills. Even if the evolution of post-consumer waste treatment has increase in recycling of 100%, in energy recovery of 77% and a decrease in landfill disposal of 44%, since 2006 [3], the goal of zero landfilling fundamental to achieve the circular economy of plastics, is still far away. As estimated by Plastic Europe, from the total amount of 29.1 million tons of plastic waste collected in Europe in 2018, 42.6% was treated for energy recovery, 32.5% was recycled and 24.9% was disposed in landfills [3].

As mentioned above, the most important demand for end-user market is represented by packaging, with an annually request of approximately 20 Million tons. This field of application, with its natural characteristic of single-use, obviously represents the main source of plastic waste, with a total amount of 17.8 Mt collected in 2018. This represents about 60% of total amount of plastic waste, and the vast majority of this post-consumer waste was recycled.

Thus, improving recycling and energy recovery are not the only solutions to the plastic pollution problem. In the recent decades, strong attention was paid to the production of plastics from renewable resources. In the long term, the world would see a decoupling of plastic production from fossil resources. As a result, the greater part of plastics will be produced from alternative feedstocks in the future, such as recovered oils or secondary plastics, responsibly sourced biomass, or even CO<sub>2</sub>.

According to European Bioplastics, a plastic material is defined bioplastic if it is bio-based (i.e. produced from biomasses such as corn starch or sugarcane), biodegradable (i.e. can be converted into water, carbon dioxide and compost from microorganisms present in nature) or presents both features at the same time.

Following the combinations of these two features, bioplastics can be classified into three main groups: i) bio-based non-biodegradable plastics, such as bio-based polypropylene (PP), or polyethylene terephthalate (PET); ii) plastics that are both bio-based and biodegradable, like polylactic acid (PLA) and polyhydroxyalkanoates (PHA); and iii) fossil-based biodegradable plastics, as poly(butylene adipate-co-terephthalate) (PBAT).

Production of bioplastics still represents 1% of the total produced plastics, but the bioplastics market is predicted to fast grow in the near future. As stated by European Bioplastics in collaboration with Nova-Institute, the global production capacities of bioplastics are predicted to grow from around 2.11 million tons in 2019 to approximately 7.6 million tons by 2026 [5].

Bioplastics have significant potential as their mechanical and thermal properties are comparable to those of oil-based plastics and can be easily altered to impart desirable attributes [6]. This, coupled to a processing involving a simple adjust of the process parameters of conventional plastic processing technologies, gives a wide range of disposal options for bioplastics. Figure 1.3 reports the global production capacities of bioplastics in 2021. The largest market segment for bioplastics is packaging with 48%, comprising both flexible and rigid packaging, followed by consumer products, textiles agriculture and automotive.



Figure 1.3. Global production capacities of bioplastics 2021 by market segment. Source: European Bioplastics

Initially, numerous alternative or bio-based plastics were produced from agricultural product such as potatoes, corn and sugarcane [7]. But, owing to the wish to save the land for food production,

the focus of the research for bio-based polymers precursors moved from food-based feedstocks to biomasses and renewable resources.

Non-biodegradable bioplastics can be recycled or incinerated like the fossil based traditional plastics [8] thus biodegradability is an important motivation for the progress of bio-based polymers. Nowadays many researchers are focusing on development of bio-based and biodegradable plastics which can be degraded through microbial activity by composting them at domestic or industrial scale creating a paradigm for a zero-waste circular economy [9] with a biodegradability that is determined based on the route and rate of degradation [10].

In conclusion, plastics have provided innovative solutions to society's ever-changing requirements and demands. After one century of history, allow humans to reach a wide range of functional and aesthetic necessities, improving the quality of life. Regrettably, plastics carry with improvements in lifestyles also the awful drawback of pollution due to the large use of this material, coupled with its hard waste disposal. Global politics and science is looking for a solution, working to solve this issue by increasing recycling, reuse and reduction in use of oil-based, non-biodegradable plastics. About this, bioplastics represents a high potential material in solving the pollution problem.

European Commission has recognized the important role of bio-plastics in the bio-economy and their importance in reaching the circular economy of plastics. Research on bioplastics is still growing, working to improve their properties and processing to reach the high performances of conventional plastics.

### **1.2 Poly (L-lactic acid)**

Poly (L-lactic acid) (PLLA) is an aliphatic thermoplastic bio-based polyester, produced from renewable resources such as corn starch and sugar beets [11–13]. It is derived from lactic acid (LA), an organic molecule naturally produced from plants, animals and microorganisms [14]. Its attractiveness is due to its physical properties similar to those of many petroleum-based plastics, and to its biodegradability to carbon dioxide, water, and humus-like matter [11,15–17].

LA was first extracted in 1780 by the Swedish scientist C.W. Scheele in sour milk, but its industrial production started after 1881, when it was obtained by fermentation [18]. LA is the simplest 2-hydroxycarboxylic acid with a carbon atom, thus exists in two enantiomeric forms, L-LA and D-LA, as shown in Figure 1.4 [19].



Figure 1.4. Structures of L- and D-Lactic Acid

Generally, LA can be produced chemically from hydrolysis of acrylonitrile, resulting in a racemic mixture of the two optical isomers [20], or from fermentation of sugars. Sugars used for LA fermentation include starch, lactose, glucose and maltose produced by corn and potatoes resulting in optically pure products [21].

The first attempt of polymerization of LA was attempted in 1845 through the polycondensation of LA by the French chemist Pelouze in 1845. This process leaded to PLLA with low molecular weight ranging from 800 to 5000 g/mol [22]. In 1932 W.H. Carothers, Du Pont's chemist inventor of nylon, improved the production process. In two hours at 250-270°C, LA was transformed in a resinous mass with an approximate molecular weight of 3,000 Da [23]. In 1954 Du Pont produced a high molecular weight PLLA and applied for patent Carother's invention with the aim of enter the industrial production. The high costs limited the production of PLLA until 1989, when P. Gruber developed for Cargill Inc. key processes for conversion of LA into lactide, and processes and technologies for purification and polymerization/devolatilization of lactide [24]. Then, production of PLLA became massive. According to Grand View Research, the global PLLA market size was valued at USD 525.47 million in 2020, and it is expected to grow at a compound annual growth rate of 18.1% from 2021 to 2028 [25].

The main synthesis routes of PLLA, via direct condensation, or azeotropic dehydration condensation from LA, or a two-step synthesis via lactide formation and ring opening polymerization from lactide, are sketched in Figure 1.5.



Figure 1.5. Synthetic pathways for the production of PLLA from LA

The direct condensation is an equilibrium reaction, thus is difficult to remove trace of water in the late stages of polymerization which limit the ultimate molecular weight achievable by this approach [11]. To solve this issue, Mitsui Toatsu Chemical patented in 1995 an azeotropic distillation process using a high-boiling solvent to directly remove water during the esterification process [26]. However, high molecular weight PLLA is mostly produced via ring opening polymerization of dimer lactide [21,27–29].

PLLA is currently used in many application fields thanks to its cost-property balance [2] and for its good processability and biocompatibility. PLLA has a melting point ( $T_m$ ) of 155-180°C and a glass transition temperature ( $T_g$ ) of 55-65°C [19,30–32]. The thermal degradation temperature of PLLA is estimated around 307-310°C [33]. Deriving from a chiral monomer, PLLA has a chirality at  $\alpha$ -carbon atom of the LA (see Figure 1.4), hence L- and D- isomers and a racemic mixture of the two are possible. Commercial PLLA grades commonly consist of a mixture of D- and L-LA with a D- LA content of 2-4% making PLLA a random copolymer with chemical and physical properties that can vary because of the chiral carbon atom. A wide range of thermal and mechanical properties and degradation rates can be achieved just by varying the composition of the copolymers or the molecular weight. As an example, by decreasing L- isomer content, the melting temperature decreases; in fact, a PLLA copolymer with a 4% of D- isomer has a  $T_m$  of 155-160°C and a  $T_g$  of 55-60 °C [34].

PLLA can biodegrade in nature by hydrolysis (both enzymatic and non-enzymatic) [35–37] to water, carbon dioxide and humus-like matter and in the human body to the natural metabolite L–LA, thanks to the ester groups in its chain that make the polymer susceptible to enzymatic attack [38] and can undergo to hydrolysis. The degradation rate is dependent on chirality [22], on molecular weight and on crystal structure and morphology [39]. The large influence of crystallinity on properties and degradation of PLLA brought to wide research efforts on crystallization kinetics and crystal morphology.

Upon different thermal and mechanical treatments, PLLA can crystallize in three structural form named  $\alpha$ -,  $\beta$ -, and  $\gamma$ -, with different helix conformation and cell symmetries.  $\alpha$ -form is the most stable and develops upon melt or cold crystallization and from solution spinning [40]. The conformation is a left-handed 10<sub>3</sub> helix packed in an orthorhombic unit cell [41]. Upon mechanical stretching, PLLA crystallizes in  $\beta$ -modification. Uncertainties are still present on the structure of the  $\beta$ -form, the latest hypothesis reports a frustrated packing of three 3<sub>1</sub> helix chains in a trigonal unit cell [42].  $\gamma$ -form is obtained via epitaxial crystallization on hexamethylbenzene substrate and is characterized by two antiparallel helices with 3<sub>1</sub> conformation packed in an orthorhombic unit cell [43]. Besides these three main structural form, PLLA exhibits also two disordered structural  $\alpha$ -forms, named  $\alpha'$ - and  $\alpha''$ -. The  $\alpha'$ -form has conformational disorder (condis crystal) and grows upon melt or cold crystallization at low temperatures, below 110-120 °C [40,44–47], whereas crystallization at higher temperatures leads to formation of  $\alpha$ -modification.  $\alpha''$ -modification, often addressed as PLLA mesophase, has much larger degree of disorder; it can develop upon mechanical drawing at 10 K above its  $T_g$  [48–50], in presence of chain mobility accelerators [51] or upon treatment with carbon dioxide (CO<sub>2</sub>) [52–54].

PLLA crystallization via crystal nucleation, growth and perfection has been widely studied [55–57]. As typical for semicrystalline polymers, crystal morphology is affected by crystallization path, with huge differences in morphology for crystals grown upon cold crystallization (i.e. when heated from below  $T_g$ ), or upon cooling from the melt, mostly due to the different nucleation mechanism [58,59].

Crystal nucleation can be either heterogeneous or homogeneous. if nucleation occurs on surfaces/heterogeneities, then it is called heterogeneous crystal nucleation. Heterogeneous nucleation often is energetically favored since the total interfacial stress/energy at the nucleus/melt boundary is lower than in case of homogeneous nucleation, in particular at low supercooling of the melt. The critical size of the nucleus and the free-enthalpy barrier, both decrease with melt-supercooling, that is, with increasing thermodynamic driving force for the phase transition.

If crystallization occurs at high supercooling or by heating from below the glassy state, crystallization starts from the so-called homogeneous nucleation: Small ordered entities made of a few parallel chain segments, called homogeneous crystal nuclei, aggregate until reaching a supercritical size and initiate crystal growth [58,59]. Homogeneous nucleation results in a much faster crystallization rate, with the formation of a very high number of small, less perfect crystals, and a crystallinity degree usually comparable with that attainable by crystallization upon cooling from the melt and a density about 10<sup>9</sup> times larger [60,61]. The kinetics of homogeneous nucleation has also been recently investigated for PLLA, and detailed knowledge of the effect of molar mass, chain structure on their development kinetics and thermal stability is now available.[62–65].

The slow crystallization kinetics is probably the major weak point of PLLA, as it complicates industrial processing to attain semi-crystalline products with the needed performance in terms of mechanical, thermal and transport properties [66,67]. Common procedures to improve crystallization kinetics of PLLA include variations on the formulation by addition of nucleating agents, blending with plasticizers or modifications in the chain structure as ramification by means of chain extenders.

Under industrial melt processing conditions, crystallization most often proceeds via heterogeneous nucleation. In order to enhance the crystallization rate, nucleating agents are frequently added to polymer formulation, with most commonly used nucleating agents detailed in literature reviews [33,68]. Unfortunately, most nucleating agents are not bio-based, nor biodegradable. For instance, talc is a highly efficient, as it can improve the half-time of crystallization of PLLA by more than one order of magnitude [56,69] but is not bio-based. Some bio-based compounds have been tested as nucleating agents for PLLA, revealing an ability in enhance the crystallization rate of PLLA, but with an efficiency not comparable to talc [69–71].

Crystallization rate can be enhanced also with addition of plasticizers, which shift  $T_g$  to lower temperature, increasing chain mobility, thus enhancing crystallization rates. Effective plasticizers for PLLA are also broadly studied, most common ones include Polyethylene Glycol (PEG) [72,73] Acetyl trietyl citrate (ATEC) [69], Trietyl Citrate (TEC) [74,75], Tributyl Citrate (TBC) [76,77], and also CO<sub>2</sub> [78–81].

Chain branching may also have positive effects on crystallization kinetics. The effect of chain branching on crystallization rate depends on the degree of branching and on branch length [82–85] and the crystallinity of the branched polymer can be controlled by tailoring the length of the side chains [86]. In particular, Long Chain Branching (LCB) is well known to have a significant effect on crystallization properties and even a small amount of LCB can improve crystallization kinetics and increase crystallization temperature, by increasing the number of nucleating sites [82,87–89]. The branching points, which can be regarded as a point of intersegmental connection, as well as chain directional change at branching points, are also expected to disturb the segmental mobility for the nuclei formation and/or the growth of crystallites [26], and there is a critical degree of branching below which crystallization rate of PLLA can be enhanced [25].

Crystallization kinetics of PLLA is a hot research topic, since crystal structure, fraction and morphology can strongly influence the applications of PLLA, as mentioned above. PLLA is commercially used as packaging material, or in single-use disposable items. Being biocompatible, bioresorbable and safe for contact with biological tissues, one of the main field of applications is the biomedical one. PLLA finds uses in tissue engineering [86], cardiovascular devices [87,88] and as drug delivery system [89,90]. Regarding the techniques used for processing PLLA, in the biomedical field as for skeletal tissue engineering, devices and sensing applications, the most used are 3D printing [91], electrospinning [68] and foaming [93,94]

### 1.3 Poly(L-lactic Acid) Foaming

Foams are materials made by two phases in which one is in the gaseous state. Among the existing foams, polymeric foams are widely produced because of the wide set of properties that arise from their cellular structure which give them a large range of tunable properties.

According to the Smithers' Annual Report on polymeric foam market, in 2021 the polymer foams market is estimated to reach 29,357 thousand tons and is expected to grow to 37,254 thousand tons in 2026 with a growth rate of 4.9% over this period [95]. In 2020 the largest part of the market was held with 51% by polyurethane which is used in industrial sectors such as automotive and construction, followed by the 37% of polystyrene used for packaging.

Due to the possibility of being designed, cut and fabricated to hold any shape, accommodate any weight and absorb shock to protect delicate products, among all the polymer processing, foams are one of the most used in packaging industry. As an example, polyurethane (PU) is a relatively soft foam, useful for fragile and lightweight items or for those sensitive to vibration. Conversely, expanded polystyrene (EPS) is broadly used in food packaging industry due to its low production cost, excellent properties and low weight. Besides the environmental and pollution problems caused by its extensive consumption [96], EPS can also be harmful for human, since styrene, its monomer, is a causal agent of various diseases including cancer [97–99].

Coupling such a broad market, with the need in the reduction of oil-based non-biodegradable plastics, replace the commodity polystyrene and polyurethane foams with bio-based polymeric foams would be environmentally very attractive. Among bio-based polymers used in the production of foams for packaging, biodegradable polyesters as polyvinyl alcohol and PLLA are extensively used in blends, mainly with starch, giving products with good properties [100,101].

In addition to packaging, foams produced from biodegradable polymers are widely used as sound and thermal insulators in construction but also as medical devices, as tissue scaffolds or drug delivery. However, bio-based foams still have poorer properties like water and moisture resistance, or mechanical, thermal and barrier properties, if compared to conventional oil-based polymer foams [102,103]. Thus, research is focusing on improving properties to reach the excellence of conventional plastics.

Polymer foams are generally produced by the addition of a chemical or a physical blowing agent [104]. The use of chemical blowing agent often makes the whole process and the final cell

structure hard to be controlled, hence current research is mainly focused on physical blowing agents like supercritical fluids. Most commonly used one is CO<sub>2</sub>, due to its pressure–tunable properties, which provides opportunities in controlling polymer-fluid interactions [105].

There are three main foaming technologies: extrusion foaming, bead foaming and injection molding foaming. They are all conducted by dissolving the physical blowing agent in the polymer matrix. After the dissolution of  $CO_2$ , cell nucleation and growth occurs trough a rapid pressure drop or an increase in the temperature. The thermodynamic instability generated by the process, determines the expulsion of the dissolved gas from the polymer matrix with sudden formation of bubbles. The stabilization of the cells occurs upon vitrification, or by crystallization of the polymer.

There are various key factors to be controlled to reach the success in a foaming experiment. The diffusivity of the blowing agent, which depends on molecular architecture and on chain configuration and interactions of the polymer, and influences concentration of the gas in the polymer matrix; the interfacial tension and the variation in the characteristic temperatures, i.e glass transition, crystallization and melting temperatures; rheological properties of the polymer during the whole process.

The first documented attempt of PLLA foaming was reported in 1996 by Mooney et al. [106] with batch foaming technique, followed by an early extrusion foaming conducted in 2000 by compounding PLLA and starch [107]. Starting from then, PLLA foaming has attracted interest and is commercially established with several patents as bead foams, mostly owned by Synbra Technology BV (BioFoam<sup>®</sup>) [108] and BASF SE (ecovio<sup>®</sup>EA) [109].

There is a wide range of applications for PLLA foams, such as packaging material, panels and sandwich composite cores, sound insulating element and construction [104]. The use of PLLA in foaming is limited by processing instability, caused by cleavage of the chains and decrease in molecular weight, due to thermal, oxidative and hydrolytic degradations [110]. Additional shortcomings that may limit processability of PLLA include low melt viscosity [111], low crystallization rate, brittleness and low impact resistance. Crystallization rate can be improved by using chain extenders to create a branched structure [112], blending with oligomeric PLLA [113] and compounding PLLA with different additives as plasticizers or nucleating agents [114,115] as summarized above.

The use of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) i.e. CO<sub>2</sub> at pressures and temperatures above the critical point, is not limited to physical blowing agent in foaming PLLA, but it can be used also as a medium to alter crystallization behavior of PLLA. scCO<sub>2</sub> can influence, in fact, the crystalline properties of the polymer [116–119], since it can swell and plasticize it, leading to a depression of the  $T_g$  [120]. This leads to an increase in the chain mobility at processing temperature, and then to an easier reorganization of polymer chains, which results in a faster crystallization of the polymer. Enhancing crystallinity of PLLA can improve the low melt strength, and extend the range of applications [121].

This plasticization effect of  $CO_2$  has been explained via a decrease in the activation energy required for the crystallization process while gas pressure increases [79,122,123], this means that the reduction in the interfacial tension of polymer/gas mixture, facilitates the creation of a new interphase in the amorphous phase [79].

The increased chain mobility favored by  $CO_2$  not only increases the crystallization rates of PLLA, but can also induce formation of a mesophase, named  $\alpha$ "-modification, as detailed [53] in paragraph 1.2, above. It has been demonstrated that mesophase not only accelerates crystallization of PLLA by increasing the nucleation density [54], but also influences the crystals morphology, because crystallization proceeding via  $CO_2$ -induced mesophase leads to non-spherulitic morphologies consisting of nano-rods [52].

The assortment of uses for PLLA foams depends on the morphology of the foams that can be obtained in the dimension varying from nano-foams to micro-foams, shape and distribution of cells within the material, and shape of the walls between cells. Aspects governing foam morphology are the rheological properties and the microstructure, i.e. crystal morphology and chain reorganization, of the polymer which can in turn be tuned by different strategies. Blending with different polymers, such as LDPE, to create miscible or immiscible systems altering the crystallization behavior can improve microcellular foaming behavior of the polymer [124]. Chain branching by means of chain extenders can increase PLLA molecular weight, melt viscosity and elasticity, resulting in fine and uniform foam morphology with an increase in the expansion ratio [93,125–128]. Also the introduction of stereocomplex crystallites (SC) [133] can influence foam morphology; the presence of SC enhances the melt strength of the polymer, resulting in foams with circular round cells and a reduced cell coalescence and collapse, with a wider foaming process window. The influence of stereoregularity of the chain was also studied: a decreasing the D-lactide content, the crystallization rates increase and are further enhanced by the plasticizing effect of  $CO_2$ [130] and this may result in a higher expansion ratio and smaller cells [117].

One extensively studied methodology to control the foam morphology is to add nucleating agents which, similar to what happens in the crystal nucleation, reduce the energy for the nucleation process leading to an increase in the bubbles nucleation rate [131]. The route of foaming PLLA nanocomposites is widely followed to obtain micro-foams with a high cell density, where nanoparticles included in the polymer matrix act as heterogeneous nucleating sites for bubbles. Many nucleating agents have been tested giving a favorable effect on foaming by reducing cells average diameter and enhancing cell density. As example, a PLLA composite containing 3 wt% of halloysite develops  $2*10^5$  cells/cm<sup>3</sup> [132], talc increases cell density by an order of magnitude and improves the uniformity of cell size [133], while and addition of 5 wt% of modified silica nanoparticles increases the cell density by ~ 80 times respect to neat PLLA foams [134]. Despite the favorable effect on cell nucleation obtained by compounding with additives or polymers, these methods can

alter the biodegradation and biocompatibility of the material. Then, for biomedical and better biodegrading applications, an internal nucleating agent could be ideal.

According to heterogeneous nucleation theory, crystals already present or developed upon solubilization/foaming can promote bubble nucleation during foaming [81]. CO<sub>2</sub> segregates in the interphase between crystal and amorphous fraction and the number of cells increases with spherulite density and surface area [135] with a result, in terms of expansion ratio, even better if compared to branching. When crystallized, foamed linear PLLA exhibits a higher expansion ratio compared both to the amorphous one, while crystallization on branched PLLA increases the stiffness of the polymer at low foaming temperatures and leads to a rise in the viscoelastic properties at high temperatures, resulting in a lower expansion ratio [81]. It was also found that increasing CO<sub>2</sub> pressure and saturation time, the induced crystallinity degree increases and the pore structure of foams varies with the crystallinity degree. A higher crystallinity increases the stiffness of the polymer resulting in a reduced cell growth and further expansion, while a lower amount of smaller crystals promotes both cell nucleation and growth, enhancing the expansion [140].

Tuning the induced crystallinity, different novel morphologies can be obtained, such as layered, core-skin and interconnected structures [136]. The dimension and morphology of the crystals are significant in the cellular structure; larger spherulites lead to round objects surrounded by elongated cells, while smaller spherulites cause stamen like cells [137]. Controlling the saturation temperature or pressure affects crystal morphology. Formation of spherulites at low crystallization temperatures (80 - 100 °C) leads to a uniform and closed cell structure, while increasing foaming temperature to 120 °C the unstable crystalline structure disappeared and an open cell structure has obtained [138]. This is due to the various crystal modifications which can develop in dependence of thermal history [139]; the efficiency of cell nucleation changes for different degrees of crystal perfection and crystal forms. Imperfect  $\alpha'$ -crystals grown in presence of CO<sub>2</sub> lead to a more efficient cell nucleation respect to that exerted by more regular  $\alpha$ -crystal. After cell nucleation on the surface of imperfect  $\alpha'$ -crystals nano-cellular foams have been obtained, with a micro/nano transition temperature for PLLA at 117 °C [140].

The results reported until this point, could let the reader look at the broadening of crystallization window and the enhancement in crystallization rates of PLLA as the perfect route to improve foaming efficiency. Unfortunately, an increase in the crystal fraction, favored by dissolution of the foaming agent at high pressure, can interfere with foam formation [116,135,136] reducing the sorption of  $scCO_2$  and increasing the stiffness of the polymer which hinders expansion [141].

Despite the efficiency of prior crystallization of the polymer in promoting bubble nucleation, the crystal fraction should be not too high, as it can hinder cell expansion. An ideal situation would imply partial ordering of the polymer, with a high number of crystals able to promote onset of foaming, whose dimension is so small that the overall crystal fraction before foaming process is limited. Such ideal situation may be attained with formation of very small ordered chain aggregates, with large surface/volume ratio, not leading to sizable crystallinity, but able to promote bubble growth. One example may be provided by homogeneous crystal nuclei (HCN). HCN, detailed in Section 1.2, are small parallel chain aggregates that develop upon annealing semicrystalline polymers, including PLLA, at temperatures close to  $T_g$ , and can act as nucleation sites for crystal growth, generating a large number of crystals with a high surface/volume ratio. The most important characteristic of homogeneous crystal nuclei is a negligible initial crystallinity of the polymer containing HCN [55], because at nucleation temperature crystal growth is almost negligible and the developed crystal fraction is not even measurable [142].

Another type of ordered structure with large surface/volume ratio is PLLA mesophase, also discussed in Section 1.2, which develops in a nanorod morphology that is maintained upon transition to stable  $\alpha$ -crystals. This difference in the crystal morphology is expected to influence foaming.

### **1.3 Aim of the work**

Starting from the need to find an ecological and economic solution to improve the properties of biodegradable polymers and to optimize the morphology of their foamed products and make them comparable to the efficiency of common plastics, the aim of this thesis is to offer a methodology that allows to tune these characteristics quickly and without adding external components to PLLA.

The strategy is to modify both the crystallization properties of the polymer and the morphology of the foam, by exploiting thermally-induced chain reorganization and the interactions between polymer chains and  $CO_2$ . This work focuses on the influence of internal nucleating agents to enhance both crystallization and bubble nucleation, exploiting the interplay between crystals and bubble nucleation in foaming PLLA with  $CO_2$ .

In Chapter 2, a study on the influence of radical branching on the crystallization kinetics of PLLA is described. Optically pure PLLA short chains, with low molecular weight were radically branched to a commercial poorly crystallizing PLLA. The efficiency of the grafting reaction was evaluated, and the influence of branching on crystallization rates and crystal nucleation efficiency was studied. The optically pure branches act as molecular nucleating agents, leading to a cooperative crystallization which enhances the crystallization rates of the polymer. In other words, this represents a successful attempt to improve thermal properties of PLLA without the use of different chemicals.

In Chapter 3, the study focuses on exploiting homogeneous crystal nuclei as heterogeneous nucleation sites for bubbles. A method to produce a mono material PLLA foam with a morphology tunable just by a thermal pre-treatment is presented. After an evaluation of nuclei density and on their influence on crystal fraction of the polymer, homogeneous crystal nuclei as enhancers in PLLA physical foaming are studied to understand their influence on foam morphology and expansion ratios.

In Chapter 4, the work goes on the other side of the mirror and focuses on the influence of  $CO_2$  on crystallization behavior of PLLA. Preliminary results on kinetics of mesophase growth as a function of gas pressure and sorption time are reported, and the interplay between the mesophase and homogeneous crystal nuclei on crystallization kinetics are studied. Due to the need of an optimal thermal control, also the design of a new batch foaming reactor is presented.

### **1.4 References**

- [1] E.G. Yarsley, V. E. Couzens, Plastics, Middlesex: Penguin Books Limited, 1945.
- G. Cecchin, G. Morini, F. Piemontesi, Ziegler-Natta Catalysts, in: Kirk-Othmer Encycl.
   Chem. Technol., John Wiley & Sons, Ltd, 2003. https://doi.org/https://doi.org/10.1002/0471238961.2609050703050303.a01.
- [3] Plastics The Facts 2020. An analysis of European plastics production, demand and waste data., (n.d.). https://plasticseurope.org/it/knowledge-hub/plastics-the-facts-2020/.
- [4] A.L. Andrady, M.A. Neal, Applications and societal benefits of plastics, Philos. Trans. R.
   Soc. B Biol. Sci. 364 (2009) 1977–1984.
- [5] European Bioplastics Global production capacities of bioplastics 2021-2026, 2021. https://www.european-bioplastics.org/wpcontent/uploads/2021/11/Global Prod Capacity Total 2020to2026.jpg.
- S.J. Rijpkema, S.G.H.A. Langens, M.R. van der Kolk, K. Gavriel, B.J. Toebes, D.A. Wilson, Modular approach to the functionalization of polymersomes, Biomacromolecules. 21 (2020) 1853–1864.
- [7] E. Piorkowska, Overview of biobased polymers, Therm. Prop. Bio-Based Polym. (2019) 1– 35.
- [8] P. Rai, S. Mehrotra, S. Priya, E. Gnansounou, S.K. Sharma, Recent advances in the sustainable design and applications of biodegradable polymers, Bioresour. Technol. 325 (2021) 124739. https://doi.org/https://doi.org/10.1016/j.biortech.2021.124739.
- [9] H. Karan, C. Funk, M. Grabert, M. Oey, B. Hankamer, Green bioplastics as part of a circular bioeconomy, Trends Plant Sci. 24 (2019) 237–249.
- [10] T. Narancic, F. Cerrone, N. Beagan, K.E. O'Connor, Recent advances in bioplastics: application and biodegradation, Polymers (Basel). 12 (2020) 920.
- [11] R.E. Drumright, P.R. Gruber, D.E. Henton, Polylactic acid technology, Adv. Mater. (2000). https://doi.org/10.1002/1521-4095(200012)12:23<1841::AID-ADMA1841>3.0.CO;2-E.
- [12] M.G. Adsul, A.J. Varma, D. V Gokhale, Lactic acid production from waste sugarcane bagasse derived cellulose, Green Chem. 9 (2007) 58–62.
- [13] M. Singhvi, D. Joshi, M. Adsul, A. Varma, D. Gokhale, D-(-)-Lactic acid production from cellobiose and cellulose by Lactobacillus lactis mutant RM2-2 4, Green Chem. 12 (2010) 1106–1109.
- [14] A. Södergård, M. Stolt, Properties of lactic acid based polymers and their correlation with composition, Prog. Polym. Sci. 27 (2002) 1123–1163.
- [15] R. Gattin, A. Copinet, C. Bertrand, Y. Couturier, Biodegradation study of a coextruded starch

and poly(lactic acid) material in various media, J. Appl. Polym. Sci. (2003). https://doi.org/10.1002/app.11701.

- G. Gorrasi, R. Pantani, Hydrolysis and Biodegradation of Poly(lactic acid), in: M.L. Di Lorenzo, R. Androsch (Eds.), Synth. Struct. Prop. Poly(Lactic Acid), Springer International Publishing, Cham, 2018: pp. 119–151. https://doi.org/10.1007/12\_2016\_12.
- [17] R.N. Darie-Niţə, C. Vasile, A. Irimia, R. Lipşa, M. Râpə, Evaluation of some eco-friendly plasticizers for PLA films processing, J. Appl. Polym. Sci. (2016). https://doi.org/10.1002/app.43223.
- [18] F.A. Castillo Martinez, E.M. Balciunas, J.M. Salgado, J.M. Domínguez González, A. Converti, R.P. de Souza Oliveira, Lactic acid properties, applications and production: A review, Trends Food Sci. Technol. 30 (2013) 70–83. https://doi.org/https://doi.org/10.1016/j.tifs.2012.11.007.
- [19] A.P. Gupta, V. Kumar, New emerging trends in synthetic biodegradable polymers Polylactide: A critique, Eur. Polym. J. 43 (2007) 4053–4074. https://doi.org/https://doi.org/10.1016/j.eurpolymj.2007.06.045.
- [20] Y. Wang, Y. Tashiro, K. Sonomoto, Fermentative production of lactic acid from renewable materials: Recent achievements, prospects, and limits, J. Biosci. Bioeng. (2015). https://doi.org/10.1016/j.jbiosc.2014.06.003.
- [21] J. Tan, M.A. Abdel-Rahman, K. Sonomoto, Biorefinery-based lactic acid fermentation: microbial production of pure monomer product, Synth. Struct. Prop. Poly (Lactic Acid). (2017) 27–66. https://doi.org/10.1007/12\_2016\_11.
- [22] D. da Silva, M. Kaduri, M. Poley, O. Adir, N. Krinsky, J. Shainsky-Roitman, A. Schroeder, Biocompatibility, biodegradation and excretion of polylactic acid (PLA) in medical implants and theranostic systems, Chem. Eng. J. 340 (2018) 9–14. https://doi.org/https://doi.org/10.1016/j.cej.2018.01.010.
- [23] W.H. Carothers, G.L. Dorough, F.J. van Natta, Studies of polymerization and ring formation.
   X. The reversible polymerization of six-membered cyclic esthers, J. Am. Chem. Soc. 54 (1932) 761–772. https://doi.org/10.1021/ja01341a046.
- [24] E.T.H. Vink, K.R. Rábago, D.A. Glassner, P.R. Gruber, Applications of life cycle assessment to NatureWorks<sup>TM</sup> polylactide (PLA) production, Polym. Degrad. Stab. 80 (2003) 403–419. https://doi.org/https://doi.org/10.1016/S0141-3910(02)00372-5.
- [25] Polylactic Acid Market Size, Share & Trends Analysis Report By End-use (Packaging, Textile, Agriculture, Automotive & Transport, Electronics), By Region (North America, APAC, Europe), And Segment Forecasts, 2021 - 2028, (2021). https://www.grandviewresearch.com/industry-analysis/polylactic-acid-pla-market.
- [26] K. Enomoto, M. Ajioka, A. Yamaguchi, Polyhydroxycarboxylic acid and preparation process

thereof, US5310865A, 1995.

- [27] A. Longo, G. Dal Poggetto, M. Malinconico, P. Laurienzo, E. Di Maio, M.L. Di Lorenzo, Enhancement of crystallization kinetics of poly(L-lactic acid) by grafting with optically pure branches, Polymer (Guildf). 227 (2021) 123852.
- [28] J.A. Byers, A.B. Biernesser, K.R. Delle Chiaie, A. Kaur, J.A. Kehl, Catalytic systems for the production of poly(lactic acid), in: Adv. Polym. Sci., 2018. https://doi.org/10.1007/12\_2017\_20.
- [29] R. Mehta, V. Kumar, H. Bhunia, S.N. Upadhyay, Synthesis of poly(lactic acid): A review, J. Macromol. Sci. Polym. Rev. (2005). https://doi.org/10.1080/15321790500304148.
- [30] Y. Kim, J.G. Verkade, Novel titanatranes with different ring sizes: syntheses, structures, and lactide polymerization catalytic capabilities, Organometallics. 21 (2002) 2395–2399.
- [31] N. Emig, H. Nguyen, H. Krautscheid, R. Réau, J.-B. Cazaux, G. Bertrand, Neutral and cationic tetracoordinated aluminum complexes featuring tridentate nitrogen donors: synthesis, structure, and catalytic activity for the ring-opening polymerization of propylene oxide and (D,L)-lactide, Organometallics. 17 (1998) 3599–3608.
- [32] C. Wang, H. Li, X. Zhao, Ring opening polymerization of L-lactide initiated by creatinine, Biomaterials. 25 (2004) 5797–5801.
- [33] D. Garlotta, A literature review of poly (lactic acid), J. Polym. Environ. 9 (2001) 63-84.
- [34] Luminy LX175 Product Data Sheet, revised 1 Sept 2017., (n.d.).
- [35] E.W. Fischer, H.J. Sterzel, G. Wegner, Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions, Kolloid-Zeitschrift Und Zeitschrift Für Polym. 251 (1973) 980–990.
- [36] T. Iwata, Y. Doi, Morphology and enzymatic degradation of poly (L-lactic acid) single crystals, Macromolecules. 31 (1998) 2461–2467.
- [37] M.S. Reeve, S.P. McCarthy, M.J. Downey, R.A. Gross, Polylactide stereochemistry: effect on enzymic degradability, Macromolecules. 27 (1994) 825–831.
- [38] D. Zhang, M.A. Kandadai, J. Cech, S. Roth, S.A. Curran, Poly(L-lactide) (PLLA)/Multiwalled Carbon Nanotube (MWCNT) Composite: Characterization and Biocompatibility Evaluation, J. Phys. Chem. B. 110 (2006) 12910–12915. https://doi.org/10.1021/jp061628k.
- [39] J.F. Turner, A. Riga, A. O'Connor, J. Zhang, J. Collis, Characterization of drawn and undrawn poly-L-lactide films by differential scanning calorimetry, J. Therm. Anal. Calorim. 75 (2004) 257–268. https://doi.org/10.1023/B:JTAN.0000017347.08469.b1.
- [40] W. Hoogsteen, A.R. Postema, A.J. Pennings, G. Ten Brinke, P. Zugenmaier, Crystal structure, conformation and morphology of solution-spun poly (L-lactide) fibers,

Macromolecules. 23 (1990) 634-642.

- [41] P. De Santis, A.J. Kovacs, Molecular conformation of poly (S-lactic acid), Biopolym. Orig. Res. Biomol. 6 (1968) 299–306.
- [42] J. Puiggali, Y. Ikada, H. Tsuji, L. Cartier, T. Okihara, B. Lotz, The frustrated structure of poly (L-lactide), Polymer (Guildf). 41 (2000) 8921–8930.
- [43] L. Cartier, T. Okihara, Y. Ikada, H. Tsuji, J. Puiggali, B. Lotz, Epitaxial crystallization and crystalline polymorphism of polylactides, Polymer (Guildf). 41 (2000) 8909–8919.
- [44] M. Cocca, M.L. Di Lorenzo, M. Malinconico, V. Frezza, Influence of crystal polymorphism on mechanical and barrier properties of poly(L-lactic acid), Eur. Polym. J. (2011). https://doi.org/10.1016/j.eurpolymj.2011.02.009.
- [45] J. Zhang, K. Tashiro, A.J. Domb, H. Tsuji, Confirmation of disorder α form of poly (L-lactic acid) by the X-ray fiber pattern and polarized IR/Raman spectra measured for uniaxiallyoriented samples, in: Macromol. Symp., Wiley Online Library, 2006: pp. 274–278.
- [46] T. Kawai, N. Rahman, G. Matsuba, K. Nishida, T. Kanaya, M. Nakano, H. Okamoto, J. Kawada, A. Usuki, N. Honma, Crystallization and melting behavior of poly (L-lactic acid), Macromolecules. 40 (2007) 9463–9469.
- [47] P. Pan, W. Kai, B. Zhu, T. Dong, Y. Inoue, Polymorphous crystallization and multiple melting behavior of poly (L-lactide): molecular weight dependence, Macromolecules. 40 (2007) 6898–6905.
- [48] G. Stoclet, R. Seguela, J.-M. Lefebvre, C. Rochas, New Insights on the Strain-Induced Mesophase of Poly(D,L-lactide): In Situ WAXS and DSC Study of the Thermo-Mechanical Stability, Macromolecules. 43 (2010) 7228–7237. https://doi.org/10.1021/ma101430c.
- [49] J. Hu, T. Zhang, M. Gu, X. Chen, J. Zhang, Spectroscopic analysis on cold drawing-induced PLLA mesophase, Polymer (Guildf). 53 (2012) 4922–4926.
- [50] T. Zhang, J. Hu, Y. Duan, F. Pi, J. Zhang, Physical Aging Enhanced Mesomorphic Structure in Melt-Quenched Poly(L-lactic acid), J. Phys. Chem. B. 115 (2011) 13835–13841. https://doi.org/10.1021/jp2087863.
- [51] J. Zhang, Y. Duan, A.J. Domb, Y. Ozaki, PLLA Mesophase and Its Phase Transition Behavior in the PLLA-PEG-PLLA Copolymer As Revealed by Infrared Spectroscopy, Macromolecules. 43 (2010) 4240–4246. https://doi.org/10.1021/ma100301h.
- [52] Q. Lan, Y. Li, Mesophase-Mediated Crystallization of Poly(L-lactide): Deterministic Pathways to Nanostructured Morphology and Superstructure Control, Macromolecules. 49 (2016) 7387–7399. https://doi.org/10.1021/acs.macromol.6b01442.
- [53] S. Li, T. Chen, X. Liao, W. Han, Z. Yan, J. Li, G. Li, Effect of Macromolecular Chain Movement and the Interchain Interaction on Crystalline Nucleation and Spherulite Growth of Polylactic Acid under High-Pressure CO<sub>2</sub>, Macromolecules. 53 (2020) 312–322.

https://doi.org/10.1021/acs.macromol.9b01601.

- [54] Q. Lan, Y. Li, H. Chi, Highly Enhanced Mesophase Formation in Glassy Poly(L-lactide) at Low Temperatures by Low-Pressure CO<sub>2</sub> That Provides Moderately Increased Molecular Mobility, Macromolecules. 49 (2016) 2262–2271. https://doi.org/10.1021/acs.macromol.6b00044.
- [55] R. Androsch, M.L. Di Lorenzo, C. Schick, Kinetics of Nucleation and Growth of Crystals of Poly(L-lactic) acid, in: Synth. Struct. Prop. Poly(Lactic Acid), 2018.
- [56] S. Saeidlou, M.A. Huneault, H. Li, C.B. Park, Poly (lactic acid) crystallization, Prog. Polym. Sci. 37 (2012) 1657–1677.
- [57] H. Tsuji, Quiescent Crystallization of Poly (Lactic Acid) and Its Copolymers-Based Materials, Therm. Prop. Bio-Based Polym. (2019) 37–86.
- [58] E. Schulz, B. Wunderlich. Macromolecular physics, vol. 2 crystal nucleation, growth, annealing. Academic Press New York 1976, Wiley Online Library, 1977.
- [59] L. Mandelkern, Crystallization of Polymers: Volume 2, Kinetics and Mechanisms, Cambridge University Press, 2004.
- [60] R. Androsch, B. Wunderlich, The link between rigid amorphous fraction and crystal perfection in cold-crystallized poly (ethylene terephthalate), Polymer (Guildf). 46 (2005) 12556–12566.
- [61] R. Androsch, A.M. Rhoades, I. Stolte, C. Schick, Density of heterogeneous and homogeneous crystal nuclei in poly (butylene terephthalate), Eur. Polym. J. 66 (2015) 180–189.
- [62] R. Androsch, M.L. Di Lorenzo, Crystal nucleation in glassy poly(L-lactic acid), Macromolecules. (2013). https://doi.org/10.1021/ma401036j.
- [63] R. Androsch, M.L. Di Lorenzo, Kinetics of crystal nucleation of poly (L-lactic acid), Polymer (Guildf). 54 (2013) 6882–6885.
- [64] R. Androsch, M.L. Di Lorenzo, C. Schick, Crystal nucleation in random L/D-lactide copolymers, Eur. Polym. J. (2016). https://doi.org/10.1016/j.eurpolymj.2016.01.020.
- [65] R. Androsch, M.L. Di Lorenzo, C. Schick, Effect of molar mass on enthalpy relaxation and crystal nucleation of poly (L-lactic acid), Eur. Polym. J. 96 (2017) 361–369.
- [66] M.L. Di Lorenzo, R. Androsch, Synthesis, Structure and Properties of Poly(lactic acid), Springer, 2018. https://doi.org/10.1007/978-3-319-64230-7.
- [67] M.L. Di Lorenzo, R. Androsch, Industrial Applications of Poly (lactic acid), Springer, 2018.
- [68] F.-L. Jin, R.-R. Hu, S.-J. Park, Improvement of thermal behaviors of biodegradable poly(lactic acid) polymer: A review, Compos. Part B Eng. 164 (2019) 287–296. https://doi.org/https://doi.org/10.1016/j.compositesb.2018.10.078.
- [69] H. Li, M.A. Huneault, Effect of nucleation and plasticization on the crystallization of poly(lactic acid), Polymer (Guildf). 48 (2007) 6855–6866.

https://doi.org/https://doi.org/10.1016/j.polymer.2007.09.020.

- [70] A.M. Harris, E.C. Lee, Improving mechanical performance of injection molded PLA by controlling crystallinity, J. Appl. Polym. Sci. 107 (2008) 2246–2255.
- [71] A. Pei, Q. Zhou, L.A. Berglund, Functionalized cellulose nanocrystals as biobased nucleation agents in poly (L-lactide)(PLLA)–Crystallization and mechanical property effects, Compos. Sci. Technol. 70 (2010) 815–821.
- [72] I. Pillin, N. Montrelay, Y. Grohens, Thermo-mechanical characterization of plasticized PLA: Is the miscibility the only significant factor?, Polymer (Guildf). 47 (2006) 4676–4682.
- [73] O. Martin, L. Avérous, Poly(lactic acid): plasticization and properties of biodegradable multiphase systems, Polymer (Guildf). 42 (2001) 6209–6219. https://doi.org/10.1016/S0032-3861(01)00086-6.
- [74] L. V Labrecque, R.A. Kumar, V. Dave, R.A. Gross, S.P. McCarthy, Citrate esters as plasticizers for poly (lactic acid), J. Appl. Polym. Sci. 66 (1997) 1507–1513.
- [75] N. Ljungberg, B. Wesslen, The effects of plasticizers on the dynamic mechanical and thermal properties of poly (lactic acid), J. Appl. Polym. Sci. 86 (2002) 1227–1234.
- [76] N. Ljungberg, B. Wesslén, Preparation and properties of plasticized poly (lactic acid) films, Biomacromolecules. 6 (2005) 1789–1796.
- [77] N. Ljungberg, B. Wesslen, Tributyl citrate oligomers as plasticizers for poly (lactic acid): thermo-mechanical film properties and aging, Polymer (Guildf). 44 (2003) 7679–7688.
- [78] M. Nofar, A. Tabatabaei, A. Ameli, C.B. Park, Comparison of melting and crystallization behaviors of polylactide under high-pressure CO<sub>2</sub>, N<sub>2</sub>, and He, Polymer (Guildf). 54 (2013) 6471–6478. https://doi.org/https://doi.org/10.1016/j.polymer.2013.09.044.
- [79] D.C. Li, T. Liu, L. Zhao, X.S. Lian, W.K. Yuan, Foaming of poly(lactic acid) based on its nonisothermal crystallization behavior under compressed carbon dioxide, Ind. Eng. Chem. Res. 50 (2011) 1997–2007. https://doi.org/10.1021/ie101723g.
- [80] A. Tabatabaei, C.B. Park, Crystallization studies of poly (lactic acid) during extrusion foaming, Annu. Tech. Conf. - ANTEC, Conf. Proc. 2017-May (2017) 2433–2437.
- [81] Q. Ren, J. Wang, W. Zhai, S. Su, Solid state foaming of poly(lactic acid) blown with compressed CO<sub>2</sub>: Influences of long chain branching and induced crystallization on foam expansion and cell morphology, Ind. Eng. Chem. Res. 52 (2013) 13411–13421. https://doi.org/10.1021/ie402039y.
- [82] J. Liu, S. Zhang, L. Zhang, Y. Bai, Crystallization behavior of long-chain branching polylactide, Ind. Eng. Chem. Res. 51 (2012) 13670–13679.
- [83] C. Zhao, D. Wu, N.A.N. Huang, H. Zhao, Crystallization and thermal properties of PLLA comb polymer, J. Polym. Sci. Part B Polym. Phys. 46 (2008) 589–598.
- [84] H. Tsuji, T. Miyase, Y. Tezuka, S.K. Saha, Physical properties, crystallization, and spherulite

growth of linear and 3-arm poly (L-lactide) s, Biomacromolecules. 6 (2005) 244-254.

- [85] Q. Hao, F. Li, Q. Li, Y. Li, L. Jia, J. Yang, Q. Fang, A. Cao, Preparation and crystallization kinetics of new structurally well-defined star-shaped biodegradable poly (L-lactide) s initiated with diverse natural sugar alcohols, Biomacromolecules. 6 (2005) 2236–2247.
- [86] T. Ouchi, S. Ichimura, Y. Ohya, Synthesis of branched poly (lactide) using polyglycidol and thermal, mechanical properties of its solution-cast film, Polymer (Guildf). 47 (2006) 429– 434.
- [87] W. Zeng, J. Wang, Z. Feng, J.-Y. Dong, S. Yan, Morphologies of long chain branched isotactic polypropylene crystallized from melt, Colloid Polym. Sci. 284 (2005) 322–326.
- [88] J. Tian, W. Yu, C. Zhou, Crystallization behaviors of linear and long chain branched polypropylene, J. Appl. Polym. Sci. 104 (2007) 3592–3600.
- [89] J. Tian, W. Yu, C. Zhou, Crystallization kinetics of linear and long-chain branched polypropylene, J. Macromol. Sci. Part B. 45 (2006) 969–985.
- [90] W. Hadasha, D. Bezuidenhout, Poly (lactic acid) as biomaterial for cardiovascular devices and tissue engineering applications, Ind. Appl. Poly (Lactic Acid). (2017) 51–77.
- [91] S. Chung, N.P. Ingle, G.A. Montero, S.H. Kim, M.W. King, Bioresorbable elastomeric vascular tissue engineering scaffolds via melt spinning and electrospinning, Acta Biomater. 6 (2010) 1958–1967.
- [92] S. Ravi, E.L. Chaikof, Biomaterials for vascular tissue engineering, Regen. Med. 5 (2010) 107–120.
- [93] N. Salahuddin, M. Abdelwahab, M. Gaber, S. Elneanaey, Synthesis and Design of Norfloxacin drug delivery system based on PLA/TiO2 nanocomposites: Antibacterial and antitumor activities, Mater. Sci. Eng. C. 108 (2020) 110337.
- [94] R.C. Nagarwal, R. Kumar, M. Dhanawat, J.K. Pandit, Modified PLA nano in situ gel: a potential ophthalmic drug delivery system, Colloids Surfaces B Biointerfaces. 86 (2011) 28–34.
- [95] M. Van den Eynde, P. Van Puyvelde, 3D Printing of Poly (lactic acid), Ind. Appl. Poly (Lactic Acid). (2017) 139–158.
- [96] I. Bonadies, A. Longo, R. Androsch, M.L. Di Lorenzo, Biodegradable electrospun PLLA fibers containing the mosquito-repellent DEET, Eur. Polym. J. 113 (2019) 377–384. https://doi.org/10.1016/j.eurpolymj.2019.02.001.
- [97] C. Marrazzo, E. Di Maio, S. Iannace, Foaming of synthetic and natural biodegradable polymers, J. Cell. Plast. (2007). https://doi.org/10.1177/0021955X06073214.
- [98] G.G. Ferrer, A. Liedmann, M.S. Niepel, Z.-M. Liu, T. Groth, Tailoring Bulk and Surface Composition of Polylactides for Application in Engineering of Skeletal Tissues, Ind. Appl. Poly (Lactic Acid). (2017) 79–108.

- [99] Smithers, The Future of Polymer Foams to 2026, 2020.
- [100] R.P. Prabhakar, S.S. Sanket, F.I. Rauphunnisa, B.P. Rahul, Impacts of thermocol waste on marine life: a review, Int. Multidiscip. Res. J. 3 (2016) 60–68.
- [101] N.D. Gil-Jasso, E.A. Giles-Mazón, G. Soriano-Giles, E.W. Reinheimer, V. Varela-Guerrero, M.F. Ballesteros-Rivas, A methodology for recycling waste expanded polystyrene using flower essential oils, Fuel. 307 (2022) 121835.
- [102] R. Verma, K.S. Vinoda, M. Papireddy, A.N.S. Gowda, Toxic pollutants from plastic waste-a review, Procedia Environ. Sci. 35 (2016) 701–708.
- [103] M.D. Sharma, A.I. Elanjickal, J.S. Mankar, R.J. Krupadam, Assessment of cancer risk of microplastics enriched with polycyclic aromatic hydrocarbons, J. Hazard. Mater. 398 (2020) 122994.
- [104] J.S. Sohn, H.K. Kim, S.W. Kim, Y. Ryu, S.W. Cha, Biodegradable foam cushions as ecofriendly packaging materials, Sustainability. 11 (2019) 1731.
- [105] S. Mali, Biodegradable foams in the development of food packaging, in: Polym. Food Appl., Springer, 2018: pp. 329–345.
- [106] L.M. Araque, V.A. Alvarez, T.J. Gutiérrez, Composite foams made from biodegradable polymers for food packaging applications, in: Polym. Food Appl., Springer, 2018: pp. 347– 355.
- [107] F. Luzi, E. Fortunati, A. Jiménez, D. Puglia, D. Pezzolla, G. Gigliotti, J.M. Kenny, A. Chiralt, L. Torre, Production and characterization of PLA\_PBS biodegradable blends reinforced with cellulose nanocrystals extracted from hemp fibres, Ind. Crops Prod. 93 (2016) 276–289.
- [108] J.M. Julien, J.C. Quantin, J.C. Bénézet, A. Bergeret, M.F. Lacrampe, P. Krawczak, Chemical foaming extrusion of poly(lactic acid) with chain-extenders: Physical and morphological characterizations, Eur. Polym. J. 67 (2015) 40–49. https://doi.org/10.1016/j.eurpolymj.2015.03.011.
- [109] E. Di Maio, E. Kiran, Foaming of polymers with supercritical fluids and perspectives on the current knowledge gaps and challenges, J. Supercrit. Fluids. 134 (2018) 157–166.
- [110] D.J. Mooney, D.F. Baldwin, N.P. Suh, J.P. Vacanti, R. Langer, Novel approach to fabricate porous sponges of poly (D,L-lactic-co-glycolic acid) without the use of organic solvents, Biomaterials. 17 (1996) 1417–1422.
- [111] Q. Fang, M.A. Hanna, Functional properties of polylactic acid starch-based loose-fill packaging foams, Cereal Chem. 77 (2000) 779–783.
- [112] R.N. Britton, F.A.H.C. Van Doormalen, J. Noordegraaf, K. Molenveld, G.G.J. Schennink, Coated particulate expandable polylactic acid, (2012).
- [113] J. Lohmann, B.D.S. Sampath, P. Gutmann, A. Künkel, K. Hahn, A. Füssi, Process for Producing expandable pelletized Material which comprises Polylactic Acid, (2013).

- [114] H. Tsuji, I. Fukui, Enhanced thermal stability of poly (lactide) s in the melt by enantiomeric polymer blending, Polymer (Guildf). 44 (2003) 2891–2896.
- [115] L.-T. Lim, R. Auras, M. Rubino, Processing technologies for poly (lactic acid), Prog. Polym. Sci. 33 (2008) 820–852.
- [116] Y. Di, S. Iannace, E. Di Maio, L. Nicolais, Reactively modified poly (lactic acid): Properties and foam processing, Macromol. Mater. Eng. (2005). https://doi.org/10.1002/mame.200500115.
- [117] N. Burgos, D. Tolaguera, S. Fiori, A. Jiménez, Synthesis and characterization of lactic acid oligomers: Evaluation of performance as poly (lactic acid) plasticizers, J. Polym. Environ. 22 (2014) 227–235.
- [118] Y. Di, S. Iannace, E. Di Maio, L. Nicolais, Poly(lactic acid)/organoclay nanocomposites: Thermal, rheological properties and foam processing, J. Polym. Sci. Part B Polym. Phys. (2005). https://doi.org/10.1002/polb.20366.
- [119] S. Sinha Ray, Rheology of polymer/layered silicate nanocomposites, J. Ind. Eng. Chem. (2006).
- [120] W. Zhai, Y. Ko, W. Zhu, A. Wong, C.B. Park, A study of the crystallization, melting, and foaming behaviors of polylactic acid in compressed CO2, Int. J. Mol. Sci. 10 (2009) 5381– 5397. https://doi.org/10.3390/ijms10125381.
- [121] M. Mihai, M.A. Huneault, B.D. Favis, Crystallinity development in cellular poly (lactic acid) in the presence of supercritical carbon dioxide, in: Annu. Tech. Conf. - ANTEC, Conf. Proc., 2009.
- [122] X. Wang, V. Kumar, W. Li, Development of crystallization in PLA during solid-state foaming process using sub-critical CO 2, Cell. Polym. 31 (2012) 1–18. https://doi.org/10.1177/026248931203100101.
- [123] X. Liao, A.V. Nawaby, P. Whitfield, M. Day, M. Champagne, J. Denault, Layered open pore poly(L-lactic acid) nanomorphology, Biomacromolecules. (2006). https://doi.org/10.1021/bm060738u.
- [124] Z. Zhang, Y.P. Handa, CO2-assisted melting of semicrystalline polymers, Macromolecules. (1997). https://doi.org/10.1021/ma9712211.
- [125] B. Wang, T. Wan, W. Zeng, Dynamic rheology and morphology of polylactide/organic montmorillonite nanocomposites, J. Appl. Polym. Sci. 121 (2011) 1032–1039.
- [126] L. Yu, H. Liu, K. Dean, L. Chen, Cold crystallization and postmelting crystallization of PLA plasticized by compressed carbon dioxide, J. Polym. Sci. Part B Polym. Phys. 46 (2008) 2630–2636.

- M. Nofar, W. Zhu, C.B. Park, Effect of dissolved CO<sub>2</sub> on the crystallization behavior of linear and branched PLA, Polymer (Guildf). 53 (2012) 3341–3353. https://doi.org/10.1016/j.polymer.2012.04.054.
- [128] X. Wang, Y. Li, Y. Jiao, H. Zhou, X. Wang, Microcellular Foaming Behaviors of Poly (Lactic Acid)/Low-Density Polyethylene Blends Induced by Compatibilization Effect, J. Polym. Environ. 27 (2019) 1721–1734. https://doi.org/10.1007/s10924-019-01466-3.
- [129] N. Najafi, M.-C. Heuzey, P.J. Carreau, D. Therriault, C.B. Park, Rheological and foaming behavior of linear and branched polylactides, Rheol. Acta. 53 (2014) 779–790.
- [130] M. Mihai, M.A. Huneault, B.D. Favis, Rheology and extrusion foaming of chain-branched poly (lactic acid), Polym. Eng. Sci. 50 (2010) 629–642.
- [131] Y.-M. Corre, A. Maazouz, J. Duchet, J. Reignier, Batch foaming of chain extended PLA with supercritical CO<sub>2</sub>: Influence of the rheological properties and the process parameters on the cellular structure, J. Supercrit. Fluids. 58 (2011) 177–188. https://doi.org/https://doi.org/10.1016/j.supflu.2011.03.006.
- [132] M. Nerkar, J.A. Ramsay, B.A. Ramsay, M. Kontopoulou, Dramatic improvements in strain hardening and crystallization kinetics of PLA by simple reactive modification in the melt state, Macromol. Mater. Eng. 299 (2014) 1419–1424.
- [133] Z. Yan, X. Liao, G. He, S. Li, F. Guo, G. Li, Green Method to Widen the Foaming Processing Window of PLA by Introducing Stereocomplex Crystallites, Ind. Eng. Chem. Res. 58 (2019) 21466–21475. https://doi.org/10.1021/acs.iecr.9b04147.
- [134] M. Nofar, A. Ameli, C.B. Park, The thermal behavior of polylactide with different D-Lactide content in the presence of dissolved CO<sub>2</sub>, Macromol. Mater. Eng. 299 (2014) 1232–1239.
- [135] M. Nofar, C.B. Park, Poly (lactic acid) foaming, Prog. Polym. Sci. 39 (2014) 1721–1741. https://doi.org/10.1016/j.progpolymsci.2014.04.001.
- [136] B. Morlin, K. Litauszki, R. Petrény, Á. Kmetty, L. Mészáros, Characterization of polylactic acid-based nanocomposite foams with supercritical CO<sub>2</sub>, Measurement. 178 (2021) 109385.
- [137] A. Ameli, D. Jahani, M. Nofar, P.U. Jung, C.B. Park, Processing and characterization of solid and foamed injection-molded polylactide with talc, J. Cell. Plast. 49 (2013) 351–374.
- [138] E.J. Jeong, C.K. Park, S.H. Kim, Fabrication of microcellular polylactide/modified silica nanocomposite foams, J. Appl. Polym. Sci. 137 (2020) 48616.
- [139] K. Taki, D. Kitano, M. Ohshima, Effect of growing crystalline phase on bubble nucleation in poly(L-lactide)/CO<sub>2</sub> batch foaming, Ind. Eng. Chem. Res. 50 (2011) 3247–3252. https://doi.org/10.1021/ie101637f.
- [140] X. Liao, A.V. Nawaby, P.S. Whitfield, Carbon dioxide-induced crystallization in poly(Llactic acid) and its effect on foam morphologies, Polym. Int. 59 (2010) 1709–1718. https://doi.org/10.1002/pi.2910.

- [141] L.Q. Xu, H.X. Huang, Foaming of poly(lactic acid) using supercritical carbon dioxide as foaming agent: Influence of crystallinity and spherulite size on cell structure and expansion ratio, Ind. Eng. Chem. Res. 53 (2014) 2277–2286. https://doi.org/10.1021/ie403594t.
- [142] Y. Yang, X. Li, Q. Zhang, C. Xia, C. Chen, X. Chen, P. Yu, Foaming of poly(lactic acid) with supercritical CO<sub>2</sub>: The combined effect of crystallinity and crystalline morphology on cellular structure, J. Supercrit. Fluids. 145 (2019) 122–132. https://doi.org/10.1016/j.supflu.2018.12.006.
- [143] R. Auras, B. Harte, S. Selke, An overview of polylactides as packaging materials, Macromol. Biosci. (2004). https://doi.org/10.1002/mabi.200400043.
- [144] J. Ni, K. Yu, H. Zhou, J. Mi, S. Chen, X. Wang, Morphological evolution of PLA foam from microcellular to nanocellular induced by cold crystallization assisted by supercritical CO<sub>2</sub>, J. Supercrit. Fluids. 158 (2020) 104719. https://doi.org/10.1016/j.supflu.2019.104719.
- [145] X. Zhang, W. Ding, N. Zhao, J. Chen, C.B. Park, Effects of Compressed CO<sub>2</sub> and Cotton Fibers on the Crystallization and Foaming Behaviors of Polylactide, Ind. Eng. Chem. Res. 57 (2018) 2094–2104. https://doi.org/10.1021/acs.iecr.7b04139.
- [146] J.W.P. Schmelzer, A.S. Abyzov, V.M. Fokin, C. Schick, E.D. Zanotto, Crystallization of glass-forming liquids: maxima of nucleation, growth, and overall crystallization rates, J. Non. Cryst. Solids. 429 (2015) 24–32.

## Chapter 2

## Enhancement of crystallization kinetics of poly(L-lactic acid) by grafting with optically pure branches<sup>1</sup>

### **2.1 Introduction**

Poly(L-lactic acid) (PLLA) is the most extensively studied and used biodegradable and renewable thermoplastic polyester, due to its potential to replace conventional oil-based polymers [1,2]. PLLA is produced by ring-opening polymerization of lactide, the cyclic dimer of lactic acid (LA) [3–5]. The latter, 2-hydroxypropanoic acid,  $CH_3$ –CH(OH)–COOH, is a naturally occurring organic acid that was discovered in sour milk in 1780 [4]. Lactic acid has an asymmetric carbon atom, which results in two optically active forms called L-lactic acid (L-LA) and D-lactic acid (D-LA). Commercial PLLA grades are produced from a mixture of both isomers, most commonly containing 96-98% of L-isomer. The presence of both L-LA and D-LA segments in the polymer chain makes PLLA a random copolymer, hence its properties are largely affected by the co-unit content [6–8].

LA can be produced either from petrochemical resources or from annually renewable feedstocks. The first process involves hydrolysis of lactonitrile, a byproduct of acrylonitrile production, and results in a racemic L-LA / D-LA mixture, which is a severe weakness [9]. The

<sup>&</sup>lt;sup>1</sup> The work presented in this chapter has been published as: Longo A., Dal Poggetto G., Malinconico M., Laurienzo P., Di Maio E. and Di Lorenzo M.L, 2021. Enhancement of crystallization kinetics of poly(L-lactic acid) by grafting with optically pure branches. Polymer 227, 123852. DOI: https://doi.org/10.1016/j.polymer.2021.123852

second process relies on microbial fermentation and can generate almost optically pure L-LA or D-LA [4]. This process has a number of additional advantages, namely the use of renewable carbohydrate biomass as feedstock, and low energy consumption due to low temperature processing. For these reasons, almost all lactic acid produced globally comes from microbial fermentation technology.

Despite the several favorable properties, PLLA has a few drawbacks that have limited so far a wider commercial exploitation. The slow crystallization kinetics is probably the major weak point of PLLA, as it hampers the attainment of degrees of crystallinity suitable for the mechanical, thermal and transport properties, among others, required in several commercial products [1,2]. It also affects foaming, with PLLA foams being of large industrial interest for biological and medical applications (e.g., tissue engineering and medical implant materials) [10–13]. As typical for random copolymers, chain composition largely affects crystallization kinetics of PLLA, which becomes increasingly slower with the decrease of stereoregularity of the polymer chain [7,14–16]. However, the high cost of purification of the monomer limits production of highly stereoregular PLLA [4,5], i.e. of a faster crystallizing polymer.

Huge research efforts have been devoted in the latest two decades to improve crystallization kinetics of PLLA. Major successful routes include variation of formulation, eg. by the addition of nucleating agents and/or plasticizers, and a tailored chain structure, which may involve branched or multi-arm architectures that also largely affects processing and foaming behavior.

Several literature reports indicate that long-chain branching (LCB) has a significant effect on polymer crystallization, and that a small amount of LCB can increase the number of nucleus sites, resulting in a higher rate of crystallization [17–20]. In the case of PLLA, both an enhancement and a diminution of crystallization rate have been observed, determined by the degree of branching and the branch length [20–27]. The branching points, which can be regarded as a point of intersegmental connection, as well as chain directional change at branching points, are also expected to disturb the segmental mobility for the nuclei formation and/or the growth of crystallites [26], and there is a critical degree of LCB below which crystallization rate of PLLA can be enhanced [25].

Blending with oligomeric PLLA can lead to a faster crystallization rate, as it results in an enhanced chain mobility due to a decrease of the glass transition temperature ( $T_g$ ) [28,29]. Tailored blending of a poorly stereoregular, high molar mass polymer with a low molar mass one produced from pure L-LA, can exploit both favorable effects of blending with low molar mass component, and its faster crystallization rate. In fact, a marked improvement of crystallization rate was demonstrated by blending a typical commercial PLLA, with high molar mass (120 kDa) and containing 4% of D-isomer, with a PLLA grade of high stereoregularity, made of pure L-isomer, and a much lower molar mass of 4 kDa [30]. Both crystal growth rates and nucleation kinetics were sizably improved. The faster nucleation rate was linked to the easier crystallization of the regular short chains, which start

to crystallize at higher temperature than the long molecules of the high molar mass polymer, acting as crystal nuclei for the subsequent crystal growth that involves both species [30].

As mentioned above, chain branching can also have positive effects on crystallization rate, but, to our knowledge, the effects of branching on crystallization rate of PLLA has been investigated only for polymers where the branches and the main chain have the same L-LA/D-LA ratio. It may be possible that branches made of optically pure L-LA can enhance crystallization rate of a poorly stereoregular grade with high molar mass, similarly as found for the blends.

In order to compare the effect of a varied chain structure with the effect of blending, a branched PLLA was prepared using the same PLLA commercial grade of Ref. [30] as main chain, i.e. a high molar mass polymer containing 4 % D-isomer, with side branches made of pure L-LA of the same molar mass of the diluent used in Ref. [30]. The graft copolymer was prepared by initial functionalization of PLLA with itaconic anhydride (IAH), followed by reaction of grafted anhydride groups with a tailor-made hydroxyl-terminated, optically pure PLLA, with molar mass  $M_n$  4,000 Da. Itaconic anhydride was preferred to the most commonly used maleic anhydride (MAH) [31–33], not only because the C=C double bond located out of the anhydride ring makes IAH more reactive than MAH towards radical grafting, but also because IAH can be derived from renewable resources, hence the resulting graft copolymer remains fully bio-based [34,35].

Details of polymer synthesis and characterization are presented below, together with analysis of crystallization kinetics, where crystal growth and overall crystallization rates are compared to the neat polymer, as well as to a blend made of commercial PLLA containing 4 wt% of D-isomer, and optically pure PLLA with molar mass  $M_n$  4,000 Da, where the blend has the same nominal composition of the graft copolymer. The aim is to define the effects of chain architecture, apart from the influence of the same pendant groups on crystallization kinetics of PLLA

### 2.2 Materials and methods

### Materials

A commercial PLLA grade (c-PLLA) with L-isomer content of 96 % and melt-flow index of 6 (210 °C/2.16 kg), grade name PLA Lx175 [36] was kindly provided by Total Corbion (The Netherlands). Before processing, the polymer was dried in a vacuum oven overnight at a temperature of 60°C to remove excess of moisture and avoid degradation. Pure L-lactide (LLA), also kindly provided by Total Corbion (The Netherlands), was dried, prior to use, under high vacuum in presence of  $P_2O_5$  for 20 h. Chloroform, dichloromethane, ethanol, acetone, diethyl ether, and 1,2-dichlorobenzene were purchased from Romil as HPLC grade. Itaconic anhydride (IAH), Luperox

101 ( $L_{101}$ ), tin(II) 2-ethylexanoate (Sn(Oct)<sub>2</sub>), sodium hydride (NaH) and Disperse Red 1 (DR1) were purchased from Sigma Aldrich and used without further purifications. 1-decanol (Sigma Aldrich) was dried for 20 h over molecular sieves 3 Å before use.

### Synthesis of PLLA-g-PLLA<sub>4k</sub> copolymer

### Synthesis of hydroxyl-terminated PLLA with molar mass 4,000 Da

Hydroxyl-terminated PLLA with molar mass 4000 Da (PLLA<sub>4k</sub>) was synthesized by ringopening polymerization using L-lactide as monomer,  $Sn(Oct)_2$  as catalyst and 1-decanol as initiator. Based on literature data [3–5], the monomer to initiator ratio was set at 27.75, with the aim to obtain a value of  $M_n$  around 4,000 Da.

In a round bottom flask, 10.09 g (0.07 mol) of LLA were charged. After monomer melting, the initiator (0.4 g, 0.0025 mol) and then the catalyst (760  $\mu$ L) were added and the reaction was carried out for 24 h at 120 °C under argon atmosphere. The product was solubilized in 15 mL of chloroform and precipitated in a large excess of ice cold diethyl ether. The final polymer was filtered and dried under vacuum overnight. (yield = 88 %).

<sup>1</sup>H-NMR: 0.88 ppm (-CH<sub>3decanol</sub>, t, 3H),1.27ppm (-CH<sub>2 decanol</sub>, m, 14H),1.58 ppm (-CH<sub>3 PLLA</sub>, d, 168H), 4.35 ppm (>C**H**-OH<sub>PLLA term</sub>, q, 1H), 5.17 ppm (-CH<sub>PLLA</sub>, q, 56H). Mn evaluated by NMR= 4104 Da.

### Functionalization of PLLA with Itaconic Anhydride by radical grafting

In order to prepare copolymers with controlled grafting degree, c-PLLA was functionalized with IAH [33,35]. Reaction was performed using a Brabender-like apparatus Rheocord EC of Haake Inc. (Vreden, Germany), using 98.7 wt% of c-PLLA, 0.8 wt% of IAH, and 0.5 wt% of peroxide  $L_{101}$ .

The reaction was carried out at 190°C and 30 rpm mixing rate. c-PLLA was loaded and melted for 2 minutes, then IAH was loaded into the chamber and the mixture was homogenized for 1 minute. Lastly, the initiator  $L_{101}$  was added and the reaction was carried out during mixing for the next 6 min. The reaction product was purified by dissolving in 1,2-dichlorobenzene (concentration 10 wt %) at 180 °C using a reflux condenser, precipitated in a large excess of ethanol and then washed in ethanol for three times to remove unreacted c-PLLA. The supernatant containing unreacted monomer (IAH) was removed by filtration and the final product was dried overnight at 60°C under vacuum.

The dried product was washed in acetone at room temperature for 48h to selectively remove low molar mass degradation products and any residues of unlinked IAH. The solvent was removed after sedimentation and the purified product (PLLA-IAH) was dried under vacuum and used for further characterization and branching reaction.

### Coupling reaction of PLLA<sub>4k</sub> with PLLA-IAH

PLLA-IAH (1.00 g, corresponding to  $4.90 \cdot 10^{-5}$  mol of IAH) was dissolved with dry dichloromethane (25mL) in a round bottom flask at 60°C under argon atmosphere. A solution of PLLA<sub>4k</sub> (0.27 g,  $5.13 \cdot 10^{-5}$  mol) in 15 mL of dichloromethane containing 0.0012 g ( $5.13 \cdot 10^{-5}$  mol) of NaH (corresponding to a molar ratio PLLA<sub>4k</sub>/NaH = 1/1) was prepared separately, and maintained under continuous stirring at room temperature until hydrogen bubbling stopped (around 20 minutes). The two solutions were then merged and stirred under argon stream at 60°C overnight. The mass ratio between PLLA-IAH and PLLA<sub>4k</sub> corresponds to 80/20 w/w. The final solution containing the crude product was first centrifuged to remove insoluble impurities, then concentrated by rotavapor and finally poured in cold hexane to precipitate the product. (yield= 90 %).

To estimate the mass of unreacted PLLA<sub>4k</sub>, and to remove any other side reactions products involving degradation of polymers, the final product was dissolved in chloroform and dialyzed in a dialysis membrane (cut-off 12,000 Da) against chloroform for 48h to ensure a complete extraction. Then the dialysis membrane was removed and the washing chloroform containing unreacted PLLA<sub>4k</sub> and any side reaction product was evaporated by rotavapor. The amount of the recovered residue was weighed and found less than 1% wt of total initial mass, indicating the high efficiency of the reaction and absence of side and degradation reactions.

### <sup>1</sup>H NMR analysis

 $^{1}$ H and  $^{13}$ C NMR spectra were recorded on a Bruker Avance DPX-400 apparatus operating at 400 MHz. Sample concentrations were about 0.7% (w/v) in CDCl<sub>3</sub>.

### Gel permeation chromatography

Gel permeation chromatography (GPC) analysis was performed with a GPC Max Viscotek equipped with a Malvern TDA with refractive index (RI), right angle laser light scattering (RALS), low angle laser light scattering (LALS) and intrinsic viscosity (*IV*) detectors. Samples were dissolved and eluted in THF (Romil) at flux of 0.8 ml min<sup>-1</sup>, with injection volume of 100  $\mu$ l, concentration of 5 mg ml<sup>-1</sup>and analyzed through a column set composed by a precolumn and two columns Phenogel Phenomenex, with exclusion limits 10<sup>6</sup> and 10<sup>3</sup> Da.

All samples were evaluated with triple point calibration (polystyrene standard  $M_n = 101,252$ Da and  $M_w = 104,959$  Da).

GPC OmniSEC software allows to evaluate the weight average number of branches per macromolecule  $(B_n)$  of a polydisperse sample and the branching frequency  $(\lambda)$  considering c-PLLA as linear reference.  $B_n$  is calculated starting from Eq. 1

$$g' = \frac{[\eta]_b}{[\eta]_l} \tag{1}$$

where g' is the intrinsic viscosity contraction factor and  $[\eta]_b$  and  $[\eta]_l$  are the intrinsic viscosities of branched and linear samples, respectively. The parameter g' is correlated to the radius of gyration contraction factor (g) by the following equation (Eq. 2)

$$g' = g^{\varepsilon} \tag{2}$$

where  $\varepsilon$  is the shape factor, which is taken to be 0.75 [37].

The relation between the number of branches per molecule  $B_n$  and the contraction factor is described by the following Zimm–Stockmayer equation (Eq. 3) [37]

$$g = \frac{6}{Bn} \left\{ \frac{1}{2} \left( \frac{2 + Bn}{Bn} \right)^{\frac{1}{2}} \ln \left[ \frac{(2 + Bn)^{\frac{1}{2}} + Bn^{\frac{1}{2}}}{(2 + Bn)^{\frac{1}{2}} - Bn^{\frac{1}{2}}} \right] - 1 \right\}$$
(3)

The branching frequency ( $\lambda$ ) is calculated as follows (Eq.4):

$$\lambda = 100R \frac{Bn}{Mw} \tag{4}$$

where R is the molecular weight of the repeating unit (72 Da) and Mw is the molecular weight of the polymer.

### Fourier Transform Infrared Spectroscopy

Functional groups characteristics of PLLA-IAH were observed via Fourier Transform Infrared Spectroscopy (FTIR), using a PerkinElmer FTIR Spectrometer Model Spectrum 100, in reflection mode. The instrument is equipped with a PerkinElmer Universal Attenuated Total Reflectance (ATR) sampling accessory with a diamond crystal. Each spectrum was determined as average of 16 individual scans, each one recorded at a resolution of 4 cm<sup>-1</sup>. Chloroform was used as solvent to prepare cast films for FTIR-ATR analyses.
#### **UV-Vis spectroscopy**

The effective amount of IAH grafted on PLLA chains was quantified via UV-Vis analysis. UV-Vis absorption spectra were recorded in the 200 - 800 nm range, at a 0.5 nm/s scan rate, using a Jasco UV-Vis spectrophotometer Mod. V570. DR1was used as chromophore.

The chromophore solution was prepared by dissolving 0.07 g of DR1 in chloroform, then stoichiometric amount of NaH was added to deprotonate DR1. Once bubbling of hydrogen stopped, this solution was mixed with 1g of PLLA-IAH in 25 ml of chloroform and the reaction was carried out for three days. The product, named PLLA-IAH-DR1, was precipitated and washed several times in cold diethyl ether until the UV-vis spectrum of the washing solution showed no more presence of dye, then vacuum dried for 24 hours at room temperature. Absorbance was measured for a solution with a concentration of  $6 * 10^{-5}$  M (20mg/mL) of PLLA-IAH-DR1, and compared with a solution at the same concentration of DR1 in chloroform. The amount of IAH grafted onto the polymer backbone was determined by means of Lambert-Beer equation:

$$A = \varepsilon b c \tag{5}$$

where A is absorbance at 475nm,  $\varepsilon$  is the molar absorption coefficient of DR1, b is the molar path that amounts to 1 cm in the specific configuration used, and c is the molar concentration of the solution. Molar absorption coefficient of DR1 was determined by measuring the absorbance of solutions at different concentration, attained by progressive dilution of a DR1/CHCl<sub>3</sub> solution with initial molar concentration of 5·10<sup>-4</sup> M (0.16mg/ml). Interpolating the absorbance values corresponding to the maximum of the absorption peak of DR1 at 475 nm, a molar absorption coefficient of DR1 in chloroform was calculated as  $\varepsilon = 8.03$  L mol<sup>-1</sup>cm<sup>-1</sup>.

#### Preparation of PLLA-IAH/PLLA<sub>4k</sub> blends

Binary blends with the same nominal composition of the branched polymer were prepared by solution casting using chloroform (0.04g/mL), to attain films with a thickness of about 200 µm. Once the solvent was evaporated, the samples were further dried under vacuum for 24 h.

# Thermal analysis

Thermal properties of the samples were investigated using a Perkin-Elmer Pyris Diamond DSC, equipped with an Intracooler II as cooling system. Temperature and energy calibration was performed with a high purity indium standard.

To analyze isothermal crystallization kinetics, the samples were melted at 200 °C for 2 min, then cooled to the desired crystallization temperature ( $T_c$ ) at 30 K min<sup>-1</sup>. The same melting conditions were used to investigate non-isothermal crystallization analysis: the various formulations were melted at 200 °C for 2 min, then cooled at 30 K min<sup>-1</sup> to 160 °C, followed by cooling at 4 K min<sup>-1</sup> to room temperature. Glass transition was analyzed after melting at 200 °C for 2 min, followed by fast cooling at the programmed rate of 100 K min<sup>-1</sup> to 0 °C, then heating at 20 K min<sup>-1</sup>.

Dry nitrogen was fluxed as purge gas at a rate of 30 mL min<sup>-1</sup>. A fresh specimen was used for each analysis. All the experiments were repeated three times to ensure reproducibility.

# **Optical microscopy**

A Zeiss Axioskop polarized-light optical microscopy (POM) and a Linkam THMS 600 hot stage were used to measure spherulite growth rates. A thin film of each sample (thickness less than 10  $\mu$ m) was obtained by squeezing between two circular Linkam cover slips on a hot stage and manually pressing. For the analysis of crystallization kinetics, the samples were melted at 200 °C for 2 min, then cooled at 30 K min<sup>-1</sup> to  $T_c$ . Nitrogen gas was fluxed in the Linkam hot stage to limit degradation.

A Scion Corporation CFW-1312C Digital Camera coupled with Image-Pro Plus 7.0 software (Media Cybernetics) was used to capture images at a pre-defined sampling rate. Spherulite radii were plotted as a function of time to obtain spherulite growth rates by linear fitting.

# 2.3 Results and Discussion

#### Synthesis and characterization of PLLA-g-PLLA<sub>4k</sub> copolymer

Functionalized PLLA can be prepared following two main strategies: ring opening polymerization (ROP) of selectively modified lactides, or post-polymerization modification [3–5]. The latter consists in preparation of new materials through modification of pre-synthetized polymer precursors, and is preferred as it allows to characterize the initial polymer before functionalization and to tune the degree of modification. In this work, a graft PLLA copolymer of predefined structure and composition was synthetized in two steps: in the first step a functional group (IAH) was introduced along the main chain of c-PLLA through radical grafting, and in the second step a presynthetized PLLA<sub>4k</sub> was covalently bonded as side branches by nucleophilic attack of the terminal hydroxyl of PLLA<sub>4k</sub>, previously activated with sodium hydride [38], to the  $\beta$ -carbonyl of anhydride, which has less steric hindrance. The synthetic route is illustrated in Figure 2.1.



Figure 2.1. Synthetic route to PLLA-g-PLLA<sub>4k</sub>

In the first step, the radical grafting of IAH was performed in a Brabender-like apparatus, operating in mild conditions with low percentages of reactants, in order to limit side reactions and degradation. This was followed by multistep purification, as detailed above, to eliminate all by-products and, in particular, low molar mass PLLA chains [34,35]. Confirmation of successful grafting was obtained by FTIR and GPC, and degree of modification was quantified by UV-Vis as discussed below.

PLLA with molecular weight around 4 kDa was synthesized by classical ROP polymerization of LLA, using 1-decanol as initiator. The molecular weight was controlled by the – OH/LLA molar ratio in the feed and calculated by the ratio between the intensities of the resonance associated with >CH–OH proton of PLLA terminal at 4.35 ppm and the resonance of -CH proton of the repeating unit at 5.17 ppm in the NMR spectrum.

The second step concerns the binding of  $PLLA_{4k}$  to the carbonyl group of IAH. Due to the purpose of the present work to make a comparison between the effect on crystallization kinetics of chain branching with respect to blending of a low amount of higher stereoregular PLLA [30], the

desired amount of  $PLLA_{4k}$  branches should not be higher than 20 wt%. Therefore, a PLLA-IAH with low amount of IAH, corresponding to 0.5 wt%, was chosen to obtain the desired branching degree.

Before the second step of synthesis, the amount of IAH grafted on PLLA chains was quantified. To prove the presence of grafted IAH on PLLA chains, PLLA-IAH was analyzed via FTIR-ATR. Unfortunately, most of IAH absorption bands overlap with PLLA ones. Absorption band at 1750 cm<sup>-1</sup> related to C=O stretching vibrations of cyclic anhydrides is fully hidden under the C=O stretching vibration of PLLA and this, together with low concentration of IAH, hampers the use of this band to prove the presence of grafted anhydride.

In order to overcome these problems, it was attempted to normalize both c-PLLA and PLLA-IAH spectra to the band at 1167 cm<sup>-1</sup> related to the C–C vibrations between  $CH_3$  and tertiary carbon of PLLA backbone. As reported in Ref. [35], where non-reacted PLLA is compared to PLLA containing 5 and 10 wt% IAH, this normalization should allow to detect an increase in the intensity of C=O stretching band from neat c-PLLA to PLLA-IAH. Unfortunately, this variation could not be appreciated in our samples, where concentration of IAH is only 0.5 wt%, too low to show a perceptible difference between the two spectra in analysis, as demonstrated in the insert of Figure 2.2.



Figure 2.2. FTIR spectra of IAH, c-PLLA and PLLA-IAH

Focusing on the wavenumber range of 2800-3100 cm<sup>-1</sup>, FTIR spectrum of PLLA-IAH shows two absorption bands at 2854 and 2925 cm<sup>-1</sup> which, according to Ref. [35], can be assigned to  $CH_{2-}$ functional groups of the grafted anhydride. Even if these bands are not present in the spectrum of pristine c-PLLA, they cannot uniquely prove the effectiveness of grafting reaction, which could be related also to  $CH_{2-}$  terminal groups generated by a chain scission reaction. However, mild polymerization conditions and a low  $[L_{101}]$  have been selected to reduce the chance of side reactions, then purification of PLLA-IAH in acetone for 48 h selectively extracts low molar mass chains, therefore most of any chain scission products are removed in this step. These considerations support the effectiveness of grafting reaction.

Figure 2.3a shows the <sup>1</sup>H NMR spectra of PLLA-IAH and PLLA-g-PLLA<sub>4k</sub>. In both spectra, besides the peaks associated to the main polymer chain [39], the small signal at 2.5 ppm (denoted as "a" in the Figure), absent in PLLA spectrum (not shown), is related to grafted IAH, as it can be attributed to the -CH<sub>2</sub>- of the anhydride ring, generally located in the region 2-3 ppm [33]. Furthermore, the absence of the resonance characteristic of  $-C=CH_2$  protons of free anhydride in the range 4.5-5.5 ppm supports the occurrence of chemical grafting of IAH on PLLA chains. In PLLAg-PLLA<sub>4k</sub> spectrum, three new peaks attributed to grafted PLLA<sub>4k</sub> are observed at 3.75, 1.27 and 0.88 ppm. The resonance at 3.75 ppm can be assigned to the -CH- proton of the terminal unit of PLLA<sub>4k</sub> conjugated to IAH (denoted as "b" in the Figure) and is specific to the occurrence of a chemical link between IAH and PLLA<sub>4k</sub> The peaks at 1.27 and 0.88 ppm are respectively attributed to -CH<sub>2</sub>- and -CH<sub>3</sub> protons deriving from 1-decanol used as ROP initiator of PLLA<sub>4k</sub>. <sup>13</sup>C NMR analysis of PLLA-g-PLLA<sub>4k</sub> confirms the occurrence of grafting and coupling reactions. The spectrum (Figure 2.3b) shows, besides main chain signals (C=O, 169.61 ppm; CH, 69.02 ppm; CH<sub>3</sub>, 16.65 ppm), the peaks relative to carbonyls (e', 169.36 and e, 169.15 ppm) and CH-CH<sub>2</sub> (d', 66.72,  $\frac{1}{2}$ and d, 65.72 ppm) of anhydride, and to aliphatic carbons from 1-decanol in PLLA<sub>4k</sub> (35-20 ppm range).

All these evidences, together with the absorption bands reported in FTIR spectrum, corroborate the efficiency of grafting and coupling reactions.



Figure 2.3a. <sup>1</sup>H NMR spectra of PLLA-IAH (black) and PLLA-g-PLLA<sub>4k</sub> (red)



Figure 2.3b.  $^{13}$ C NMR spectrum of PLLA-g-PLLA<sub>4k</sub>

Due to the low intensities of IAH signals, NMR could be not accurate for a reliable quantitative evaluation. *Liu et al.* [40] suggested an alternative method for quantification of grafted anhydride by means of UV-Vis spectroscopy. Thus, in order to determine the functionalization degree, the product was analyzed with UV-Vis spectroscopy, after conjugation of PLLA-IAH with DR1 chromophore. DR1 was chosen for the high solubility and for the presence of a reactive –OH located far from the amino-4-nitroazobenzene chromophoric unit. This feature leads to only negligible variation in terms of  $\lambda_{max}$  after reaction with PLLA<sub>4k</sub>. The reaction scheme is presented in Figure 2.4. The reaction was carried out with an excess of chromophore in order to saturate all anhydride groups with DR1. The synthesis pattern is analogous to the one previously described. DR1 was coupled to the carbonyl of anhydride *via* nucleophilic addition, after activation of the –OH group of DR1 with sodium hydride:



Figure 2.4. Synthetic pathway to PLLA-IAH-DR1

The reaction product was washed several times with diethyl ether, until the UV-Vis spectrum of the washing solution was found free of dye. This purification ensures the separation of unconjugated DR1, thus is possible to assume that the amount of DR1 determined via UV-Vis is conjugated to PLLA-IAH.

UV-Vis absorption spectra of DR1 and PLLA-IAH-DR1 are compared in Figure 2.5. Both spectra show the typical absorption band of DR1 in chloroform at wavelength 475 mm, due to interaction between azo functionality (-N=N-) and the attached aromatic moieties [41]. This

absorption peak is present both in DR1 and in the PLLA-IAH-DR1 spectra, providing evidence of the effectiveness of grafting reaction. More importantly, it allows to quantify the amount of IAH grafted onto the polymer backbone. The grafting degree of IAH on c-PLLA backbone results to be 0.5 wt%.



Figure 2.5. UV-Vis spectra of PLLA-IAH-DR1 and DR1

Further information on the efficiency of grafting reaction comes from analysis of GPC data, presented in Table 1, which compares weight-average molar mass  $(M_w)$ , number-average molar mass  $(M_n)$ , molar mass at peak of the distribution curve  $(M_p)$  and intrinsic viscosity (IV) of c-PLLA, PLLA-IAH, PLLA<sub>4k</sub> and PLLA-g-PLLA<sub>4k</sub>. Table 1 shows a sizable decrease of  $M_n$  upon addition of IAH to c-PLLA, which suggests some degree of chain degradation occurring upon functionalization reaction concerning mostly low molecular weight fraction of polymer. This behavior is confirmed by a decrease in  $M_w$  and by an increase of  $M_p$ .

Sample	$M_{ m w}$ (kDa)	$M_{\rm n}({\rm kDa})$	$M_p$ (kDa)	IV (dL/g)
c-PLLA	104	69	83	1.6
PLLA-IAH	122	33	110	0.75
PLLA <sub>4k</sub>	5.6	4.2	4.9	0.45
PLLA-g-PLLA <sub>4k</sub>	191	52	110	0.54

Table 2.1. Molar mass distribution and intrinsic viscosity of commercial and synthesized samples

Despite PLLA-g-PLLA<sub>4k</sub> shows higher values of  $M_w$  and  $M_p$  than c-PLLA, it has a lower IV suggesting the presence of branching [42]: the volume occupied by a branched structure is lower than that occupied by a linear structure, which results in a lower IV for the branched polymer. GPC data were used to derive Mark-Houwink plots, which relate molar mass to IV [43], as presented in Figure 2.6. Mark-Houwink equation describes a power law relation between molecular weight and intrinsic viscosity, which is linear in the case of linear polymers. Branched polymers display deviation from linearity related to branching [42], with the deviation increasing with the branching number.

As seen in Figure 2.6, the commercial grade (c-PLLA, green curve) shows the highest IV, due to the looser conformation in the eluent of the linear polymer (higher hydrodynamic volume) with respect to the modified polymers; grafting with itaconic anhydride (PLLA-IAH, black curve) leads to a slightly lower IV in the high  $M_w$  range, attributable to some branching arising from radical recombination mechanisms, according to ref. 35. Intrinsic viscosity further decreases upon reaction with PLLA<sub>4k</sub> (PLLA-g-PLLA<sub>4k</sub>, red curve). Not only PLLA-g-PLLA<sub>4k</sub> shows the lowest IV, but it also displays a more curved downward profile in the high molecular weight range, which is characteristic of branched polymers [42].

Branching leads to an increase in the molecular density of the polymer, which is reversely proportional to *IV*, and the radical grafting is more probable to occur for higher molecular weights. So, increasing the molecular weight, the chance of branching points increases and the differences between linear and branched polymer are more evident. Thus in the high Mw range, the Mark-Houwink line of PLLA-g-PLLA<sub>4k</sub> curves downward because the sample has a lower hydrodynamic volume due to a more compact conformation in the solvent [42] proving a higher efficiency of grafting reaction in this M<sub>w</sub> range. Furthermore, through GPC software it was possible to evaluate the average number of branches per macromolecule ( $B_n$ ) and the branching frequency ( $\lambda$ ) as 11.05 and 0.416, respectively, which correspond to an average value of one branch every 240 repeating units.



Figure 2.6. Mark-Houwink plot of c-PLLA(green), PLLA-g-PLLA<sub>4k</sub> (red)

# Thermal properties and crystallization kinetics of PLLA-g-PLLA<sub>4k</sub> copolymer

From the data reported and discussed above we can reasonably assume that the synthesized PLLA-*g*-PLLA<sub>4k</sub> sample presents a random distribution of branches made of optically pure PLLA segments, grafted onto a PLLA backbone with lower optical purity. The thermal properties and the crystallization behavior of the synthesized sample were compared to PLLA-IAH, as reference, and to a blend containing the same mass composition of the graft copolymer, i.e., made of 80 wt% of PLLA-IAH and 20 wt% of PLLA<sub>4k</sub>. The latter comparison was performed as an effort to investigate the influence of branched chain architecture on crystallization kinetics. As detailed in Ref. [30], blending c-PLLA with a highly stereoregular PLLA oligomer results in a sizable increase of both nucleation and crystal growth rates. Therefore, any measured variation in crystallization kinetics of the branched polymer may in principle be ascribed the presence of short stereoregular chains, which favor crystallization even if not covalently bonded to the main PLLA chain.

Figure 2.7 presents the thermal analysis of these PLLA-based formulations. Data were measured upon heating at 20 K min<sup>-1</sup>, after cooling at 100 K min<sup>-1</sup>. PLLA-IAH displays a glass transition ( $T_g$ ) centered at 61 °C, typical of PLLA [1], coupled to a small enthalpy relaxation endotherm due to the different heating and cooling rates used [44]. Blending PLLA-IAH with OH-terminated PLLA oligomer made of pure l-isomer units (sample coded as "blend") results in a marked decrease of  $T_g$ , down to about 55 °C, with a similar decrease in  $T_g$  observed also in the PLLA-g-PLLA<sub>4k</sub> graft copolymer (sample coded as "graft"). The measured diminution of  $T_g$  in the blend is in line with literature data of PLLA blends with comparable composition, when a high molar mass

PLLA is blended with low molar mass grades [29,30], with the latter often added to PLLA formulation as plasticizers [28,45–49]. Similar decreases of  $T_g$  have been reported also for branched polymers, compared to linear chains of similar molar mass, and arise from the higher free volume due to the increased number of chain ends in the branched architecture [50–52].



Figure 2.7. Heat flow rate plots of PLLA-based formulations, upon heating at 20 K min<sup>-1</sup>.

Above  $T_g$ , PLLA-IAH displays a broad cold crystallization exotherm, centered around 130 °C, followed by a melting peak at 153 °C. The cold crystallization exotherms of the blended and grafted formulations are markedly anticipated, compared to the linear grade, being centered around 110-112 °C. This is followed by a double melting peak at 150-160 °C, typical of PLLA containing both  $\alpha$ '- and  $\alpha$ -crystals, or  $\alpha$ '-crystals that transform to  $\alpha$ -modification upon heating [1,7,8]. The double endotherm is not seen in PLLA-IAH plot, due to the high crystallization temperature that leads to growth of  $\alpha$ -crystals [1,7,8]. The initial, qualitative indication of the faster crystallization kinetics of the samples containing short stereoregular sequences is confirmed by the DSC plots measured upon cooling at 4 K min<sup>-1</sup>, presented in Figure 2.8. The blended and grafted formulations display only minor differences in the experimental data, with a sharp crystallization exotherm appearing on cooling. Conversely, the linear polymer shows a broad and weak exotherm, which is also delayed compared to the other grades.



Figure 2.8. Heat flow rate plots of PLLA-based formulations, upon heating at 20 K min<sup>-1</sup>.

Quantitative data on overall crystallization rate of the samples are displayed in Figure 2.9, which shows the half-time of crystallization  $(\tau_{\frac{1}{2}})$  as function of the isothermal crystallization temperature ( $T_c$ ). Data are compared to commercial PLLA, as received (c-PLLA) and melt processed in Brabender mixer (c-PLLA<sub>Pr</sub>). The blended and grafted grades display a much lower crystallization time compared to the plain linear polymer, as well as to the polymer reacted with IAH, indicating their sizable faster crystallization. Data gained for the blended and grafted compositions mostly overlap within experimental uncertainty, with minor differences observed only at temperatures where the crystallization rate is lower.



Figure 2.9. Half-time of crystallization ( $\tau_{\frac{1}{2}}$ ) as function of crystallization temperature.

Comparison of the data presented in Figures 2.7-2.9 reveals that the overall crystallization rate is markedly faster in all the samples, compared to the data reported in Ref. [30], which are also displayed in Figure 2.9. It is likely that the grafting reaction with itaconic anhydride in the Brabender mixer causes unwanted incorporation of particles that act as nucleating agents for PLLA formulations. In fact, after melt processing commercial PLLA displays a much faster crystallization rate (c-PLLA<sub>Pr</sub> *vs.* c-PLLA plots). Crystallization rate data of c-PLLA<sub>Pr</sub> and PLLA-IAH overlap within experimental uncertainty, probing not only that the faster crystallization rate of PLLA-IAH compared to c-PLLA is due to melt processing, but also that PLLA-IAH can be used as reference to compare the effect of blending and grafting on crystallization kinetics.

The varied nucleation density caused by melt processing is revealed by optical microscopy analysis. The optical micrographs of PLLA-IAH prepared by Brabender mixing and of PLLA-g-PLLA<sub>4k</sub>, both dissolved in chloroform to attain cast film, are compared in Figure 2.10 to c-PLLA film attained by casting only. The micrographs refer to samples isothermally crystallized at 140 °C. A much higher nucleation density is obvious in the melt-processed samples, which causes the faster crystallization of the reacted polymer seen in Figures 2.7-2.9.



c-PLLA

PLLA-IAH

Figure 2.10. Optical micrographs (crossed polars) of PLLA formulations during isothermal crystallization at 140 °C.

The isothermal spherulite growth rates (*G*) of PLLA grafted with IAH, plain, blended with OH-terminated oligomer, and grafted with same oligomer, are presented in Figure 2.11. *G* values are limited to  $T_c \ge 115$  °C, as at lower temperatures the very high nucleation density complicates the attainment of reliable data. Experimental data are compared to spherulite growth rates of pristine c-PLLA, taken from Ref. [30], and with the same polymer after melt processing (c-PLLA<sub>Pr</sub>). *G* data of both c-PLLA and c-PLLA<sub>Pr</sub> overlap, within experimental uncertainty, with *G* values of PLLA grafted with itaconic anhydride. Not only this confirms that the much faster crystallization rate of PLLA containing anhydride units detailed above, is caused by the enhanced nucleation, but provides the

additional information that anhydride units randomly dispersed in the PLLA chains do not sizably disturb growth of PLLA crystals. Conversely, a significant increase in spherulite growth rate is observed in the blended formulation, which is even more marked in the copolymer.



Figure 2.11. Spherulite growth rates of PLLA formulations.

As demonstrated in Ref. [30], in the blended formulation the stereoregular and more mobile entangled short chains of the OH-terminated oligomer start to crystallize at a higher temperature upon cooling, or in a shorter time upon isothermal crystallization, compared to the commercial PLLA of low stereoregularity and high molar mass. These crystals act as nuclei for the growth of PLLA crystals that contain both blend components which, in turn, is also facilitated by the presence of short chains. It can be hypothesized that a similar nucleation mechanism occurs in the graft copolymer, with an initial crystallization of the highly stereoregular side chains, whose crystallization kinetics is higher than that of the chain backbone, since the latter contains d-isomer units that act as chain defects interfering with crystal ordering. After primary nucleation, also a faster spherulite growth is observed, higher in the case of graft copolymer. Both increases can be rationalized taking into account that addition of short PLLA chains results in a lower  $T_{g}$ , especially in the blends, which facilitates transport of crystallizable chains in the melt across the liquid–solid interface, due to the higher chain mobility at parity of temperature. However, the increase in *G* is even more marked in the graft copolymer than in the blend, which suggests that additional effects need to be taken into account.

For long polymer molecules, the rate determining step of crystal growth has been named 'molecular nucleation' [53]: when a new polymer molecule is added to a crystal, first a small part of it nucleates on the growing substrate, then the remaining part of the chain is drawn from the entangled melt [54]. For both blend and graft copolymer, crystallization is initiated by the short stereoregular

sequences. In the blend, once crystal nuclei made of stereoregular oligomers are developed, each long PLLA chain must attach to growing crystals (the 'molecular nucleation') before further chain ordering can lead to crystal growth. If in the graft copolymer the crystal nuclei are made of the short side chains, chemically bonded to the long PLLA backbones, the latter are already attached to the crystal surface, hence not need the molecular nucleation step for the subsequent crystal growth. This results in a faster crystal growth, as shown in Figure 2.11, even faster than in the blend, at parity of  $T_{g}$ .

In other words, the synthesis of a graft copolymer with a well-defined length and amount of side chains by means of a tailored chemistry can provide an efficient way to attain a faster crystallization rate of PLLA, even higher than that attainable for a blend with the same nominal composition.

# **2.3 Conclusions**

A PLLA with a tailored amount and length of side branches randomly distributed along the main chain was synthesized by radical functionalization with IAH and subsequent coupling with short and optically pure PLLA chains able to enhance crystallization rate. The functionalization degree, determined by UV-vis spectroscopy is 0.5 wt%. The optically pure PLLA<sub>4k</sub> branches were introduced via nucleophilic attack to the IAH and the decrease in intrinsic viscosity combined with a deviation from linearity for high molecular weight in the Mark-Houwink plot of the graft copolymer proved the presence of branching, with an average value of one branch every 240 repeating units, randomly distributed along the PLLA chain.

Chain functionalization with IAH does not sizably vary the thermal properties of the polymer, nor the crystal growth rate, and the only measurable effect of an enhanced nucleation rate is due to unwanted incorporation of impurities upon processing. Compared to a binary blend with the same nominal composition, the graft copolymer displays a higher spherulite growth rate, which was rationalized in terms of molecular nucleation. The latter is a rate-limiting step in polymer crystallization, which is not needed in the copolymer, where the optically pure short side chains that crystallize earlier act as molecular nuclei for the subsequent attachment of the main chain backbone to the crystals.

The enhancement of crystallization kinetics of poly(L-lactic acid) by copolymerization with optically pure branches has been demonstrated to date only for the chain architecture and composition detailed in this manuscript, i.e. for a graft copolymer made of side chains of  $M_n = 4,000$  randomly attached to a main chain on average every 240 repeating units. It is likely that crystallization rate of PLLA may be further improved beyond the results detailed here, by proper

variation of side chains, in terms of chain length, density and composition. Furthermore, since the glass transition is only barely affected by chain architecture and composition, even faster crystallization rate can be attained by adding specific components to the formulation, i.e. by addition of plasticizers, beyond other specific additives like nucleating agents, paving a path to overcome one the main drawbacks of PLLA that have limited so far its wider commercial exploitation.

# Acknowledgements

The authors wish to thank Total Corbion for kindly providing PLLA and LLA, as well as Dr. Salvatore Mallardo (IPCB-CNR) for the essential assistance in the use of Rheocord.

# 2.4 References

- M.L. Di Lorenzo, R. Androsch, Synthesis, Structure and Properties of Poly (lactic acid), Springer, 2018. https://doi.org/10.1007/978-3-319-64230-7.
- [2] M.L. Di Lorenzo, R. Androsch, Industrial Applications of Poly (lactic acid), 2018.
- [3] R. Mehta, V. Kumar, H. Bhunia, S.N. Upadhyay, Synthesis of poly(lactic acid): A review, J. Macromol. Sci. Polym. Rev. (2005). https://doi.org/10.1080/15321790500304148.
- [4] J. Tan, M.A. Abdel-Rahman, K. Sonomoto, Biorefinery-based lactic acid fermentation: microbial production of pure monomer product, Synth. Struct. Prop. Poly (Lactic Acid). (2017) 27–66. https://doi.org/10.1007/12 2016 11.
- J.A. Byers, A.B. Biernesser, K.R. Delle Chiaie, A. Kaur, J.A. Kehl, Catalytic systems for the production of poly(lactic acid), in: Adv. Polym. Sci., 2018. https://doi.org/10.1007/12\_2017\_20.
- [6] M.L. Di Lorenzo, P. Rubino, R. Luijkx, M. Hélou, Influence of chain structure on crystal polymorphism of poly(lactic acid). Part 1: Effect of optical purity of the monomer, Colloid Polym. Sci. (2014). https://doi.org/10.1007/s00396-013-3081-z.
- [7] M.L. Di Lorenzo, R. Androsch, Stability and Reorganization of α'-Crystals in Random L/D-Lactide Copolymers, Macromol. Chem. Phys. (2016).
   https://doi.org/10.1002/macp.201600073.
- [8] M.L. Di Lorenzo, R. Androsch, Influence of α'-/α-crystal polymorphism on properties of poly(L-lactic acid), Polym. Int. (2019). https://doi.org/10.1002/pi.5707.
- [9] Y. Wang, Y. Tashiro, K. Sonomoto, Fermentative production of lactic acid from renewable materials: Recent achievements, prospects, and limits, J. Biosci. Bioeng. (2015). https://doi.org/10.1016/j.jbiosc.2014.06.003.
- Y. Di, S. Iannace, E. Di Maio, L. Nicolais, Reactively modified poly (lactic acid): Properties and foam processing, Macromol. Mater. Eng. (2005). https://doi.org/10.1002/mame.200500115.
- [11] D.C. Li, T. Liu, L. Zhao, X.S. Lian, W.K. Yuan, Foaming of poly(lactic acid) based on its nonisothermal crystallization behavior under compressed carbon dioxide, Ind. Eng. Chem. Res. 50 (2011) 1997–2007. https://doi.org/10.1021/ie101723g.
- M. Nofar, C.B. Park, Poly (lactic acid) foaming, Prog. Polym. Sci. 39 (2014) 1721–1741. https://doi.org/10.1016/j.progpolymsci.2014.04.001.
- S. Iannace, L. Sorrentino, E. Di Maio, Biodegradable biomedical foam scaffolds, in: Biomed.
   Foam. Tissue Eng. Appl., 2014. https://doi.org/10.1533/9780857097033.1.163.
- [14] R. Androsch, M.L. Di Lorenzo, C. Schick, Crystal nucleation in random L/D-lactide

copolymers, Eur. Polym. J. (2016). https://doi.org/10.1016/j.eurpolymj.2016.01.020.

- [15] M.L. Di Lorenzo, R. Androsch, Crystallization of Poly(lactic acid), in: Biodegrad. Polyesters, John Wiley & Sons, Ltd, 2015: pp. 109–130. https://doi.org/https://doi.org/10.1002/9783527656950.ch5.
- [16] R. Androsch, M.L. Di Lorenzo, C. Schick, Kinetics of Nucleation and Growth of Crystals of Poly(L-lactic) acid, in: Synth. Struct. Prop. Poly(Lactic Acid), 2018.
- [17] W. Zeng, J. Wang, Z. Feng, J.-Y. Dong, S. Yan, Morphologies of long chain branched isotactic polypropylene crystallized from melt, Colloid Polym. Sci. 284 (2005) 322–326.
- [18] J. Tian, W. Yu, C. Zhou, Crystallization behaviors of linear and long chain branched polypropylene, J. Appl. Polym. Sci. 104 (2007) 3592–3600.
- [19] J. Tian, W. Yu, C. Zhou, Crystallization kinetics of linear and long-chain branched polypropylene, J. Macromol. Sci. Part B. 45 (2006) 969–985.
- [20] J. Liu, S. Zhang, L. Zhang, Y. Bai, Crystallization behavior of long-chain branching polylactide, Ind. Eng. Chem. Res. 51 (2012) 13670–13679.
- [21] C. Zhao, D. Wu, N.A.N. Huang, H. Zhao, Crystallization and thermal properties of PLLA comb polymer, J. Polym. Sci. Part B Polym. Phys. 46 (2008) 589–598.
- [22] H. Tsuji, T. Miyase, Y. Tezuka, S.K. Saha, Physical properties, crystallization, and spherulite growth of linear and 3-arm poly (L-lactide) s, Biomacromolecules. 6 (2005) 244–254.
- [23] Q. Hao, F. Li, Q. Li, Y. Li, L. Jia, J. Yang, Q. Fang, A. Cao, Preparation and crystallization kinetics of new structurally well-defined star-shaped biodegradable poly (L-lactide) s initiated with diverse natural sugar alcohols, Biomacromolecules. 6 (2005) 2236–2247.
- J.R. Dorgan, J.S. Williams, D.N. Lewis, Melt rheology of poly(lactic acid): Entanglement and chain architecture effects, J. Rheol. (N. Y. N. Y). (1999).
   https://doi.org/10.1122/1.551041.
- [25] N. Najafi, M.-C. Heuzey, P. Carreau, D. Therriault, Quiescent and shear-induced crystallization of linear and branched polylactides, Rheol. Acta. 54 (2015) 831–845.
- [26] H. Tsuji, Quiescent Crystallization of Poly (Lactic Acid) and Its Copolymers-Based Materials, Therm. Prop. Bio-Based Polym. (2019) 37–86.
- [27] G. Gorrasi, R. Pantani, Hydrolysis and Biodegradation of Poly(lactic acid), in: M.L. Di Lorenzo, R. Androsch (Eds.), Synth. Struct. Prop. Poly(Lactic Acid), Springer International Publishing, Cham, 2018: pp. 119–151. https://doi.org/10.1007/12\_2016\_12.
- [28] N. Burgos, D. Tolaguera, S. Fiori, A. Jiménez, Synthesis and characterization of lactic acid oligomers: Evaluation of performance as poly (lactic acid) plasticizers, J. Polym. Environ. 22 (2014) 227–235.
- [29] R. Avolio, R. Castaldo, G. Gentile, V. Ambrogi, S. Fiori, M. Avella, M. Cocca, M.E. Errico, Plasticization of poly (lactic acid) through blending with oligomers of lactic acid: effect of

the physical aging on properties, Eur. Polym. J. 66 (2015) 533-542.

- [30] M.L. Di Lorenzo, R. Androsch, Accelerated crystallization of high molar mass poly (L/Dlactic acid) by blending with low molar mass poly (L-lactic acid), Eur. Polym. J. 100 (2018) 172–177.
- [31] J. Pan, Y. Wang, S. Qin, B. Zhang, Y. Luo, Grafting reaction of poly (D, L) lactic acid with maleic anhydride and hexanediamine to introduce more reactive groups in its bulk, J. Biomed. Mater. Res. Part B Appl. Biomater. An Off. J. Soc. Biomater. Japanese Soc. Biomater. Aust. Soc. Biomater. Korean Soc. Biomater. 74 (2005) 476–480.
- [32] D. Carlson, L. Nie, R. Narayan, P. Dubois, Maleation of polylactide (PLA) by reactive extrusion, J. Appl. Polym. Sci. 72 (1999) 477–485.
- [33] S.W. Hwang, S.B. Lee, C.K. Lee, J.Y. Lee, J.K. Shim, S.E.M. Selke, H. Soto-Valdez, L. Matuana, M. Rubino, R. Auras, Grafting of maleic anhydride on poly (L-lactic acid). Effects on physical and mechanical properties, Polym. Test. 31 (2012) 333–344.
- [34] J. Petruš, F. Kučera, I. Chamradová, J. Jančář, Real-time monitoring of radical grafting of poly (lactic acid) with itaconic anhydride in melt, Eur. Polym. J. 103 (2018) 378–389.
- [35] J. Petruš, F. Kučera, J. Petrůj, Post-polymerization modification of poly (lactic acid) via radical grafting with itaconic anhydride, Eur. Polym. J. 77 (2016) 16–30.
- [36] Luminy LX175 Product Data Sheet, revised 1 Sept 2017., (n.d.).
- [37] M.N. Collins, C. Birkinshaw, Physical properties of crosslinked hyaluronic acid hydrogels.,
   J. Mater. Sci. Mater. Med. 19 (2008) 3335–3343. https://doi.org/10.1007/s10856-008-3476-4.
- [38] X. Jiang, J. Zhou, Y. Zhou, H. Sun, J. Xu, F. Feng, W. Qu, Convenient Method of Synthesizing Aryloxyalkyl Esters from Phenolic Esters Using Halogenated Alcohols, Molecules. 23 (2018) 1715. https://doi.org/10.3390/molecules23071715.
- [39] K. Suganuma, K. Horiuchi, H. Matsuda, H.N. Cheng, A. Aoki, T. Asakura, NMR analysis and chemical shift calculations of poly(lactic acid) dimer model compounds with different tacticities, Polym. J. 44 (2012) 838–844. https://doi.org/10.1038/pj.2012.106.
- [40] W. Liu, T. Liu, T. Liu, T. Liu, J. Xin, W.C. Hiscox, H. Liu, L. Liu, J. Zhang, Improving Grafting Efficiency of Dicarboxylic Anhydride Monomer on Polylactic Acid by Manipulating Monomer Structure and Using Comonomer and Reducing Agent, Ind. Eng. Chem. Res. 56 (2017) 3920–3927. https://doi.org/10.1021/acs.iecr.6b05051.
- [41] Y. Cui, M. Wang, L. Chen, G. Qian, Synthesis and spectroscopic characterization of an alkoxysilane dye containing CI Disperse Red 1, Dye. Pigment. 62 (2004) 43–47.
- [42] M. Kurata, M. Abe, M. Iwama, M. Matsushima, Randomly branched polymers. I. Hydrodynamic properties, Polym. J. 3 (1972) 729–738.

- [43] P.M. Wood-Adams, J.M. Dealy, A.W. Degroot, O.D. Redwine, Effect of molecular structure on the linear viscoelastic behavior of polyethylene, Macromolecules. 33 (2000) 7489–7499.
- [44] B. Wunderlich, Thermal Analysis, Academic Press, Inc., New York, 1990.
- [45] O. Martin, L. Avérous, Poly(lactic acid): plasticization and properties of biodegradable multiphase systems, Polymer (Guildf). 42 (2001) 6209–6219. https://doi.org/https://doi.org/10.1016/S0032-3861(01)00086-6.
- [46] J. Ambrosio-Martín, M.J. Fabra, A. Lopez-Rubio, J.M. Lagaron, An effect of lactic acid oligomers on the barrier properties of polylactide, J. Mater. Sci. 49 (2014) 2975–2986.
- [47] R.N. Darie-Niţə, C. Vasile, A. Irimia, R. Lipşa, M. Râpə, Evaluation of some eco-friendly plasticizers for PLA films processing, J. Appl. Polym. Sci. (2016). https://doi.org/10.1002/app.43223.
- [48] M.K. Fehri, C. Mugoni, P. Cinelli, I. Anguillesi, M.B. Coltelli, S. Fiori, M. Montorsi, A. Lazzeri, Composition dependence of the synergistic effect of nucleating agent and plasticizer in poly (lactic acid): A Mixture Design study, (2016).
- [49] F. Cicogna, S. Coiai, C. De Monte, R. Spiniello, S. Fiori, M. Franceschi, F. Braca, P. Cinelli, S.M.K. Fehri, A. Lazzeri, Poly (lactic acid) plasticized with low-molecular-weight polyesters: structural, thermal and biodegradability features, Polym. Int. 66 (2017) 761–769.
- Y. Tsukahara, K. Tsutsumi, Y. Okamoto, On some bulk properties of poly(macromonomer)s, Die Makromol. Chemie, Rapid Commun. 13 (1992) 409–413. https://doi.org/https://doi.org/10.1002/marc.1992.030130902.
- [51] D. Vlassopoulos, G. Fytas, B. Loppinet, F. Isel, P. Lutz, H. Benoit, Polymacromonomers: Structure and dynamics in nondilute solutions, melts, and mixtures, Macromolecules. 33 (2000) 5960–5969.
- [52] F. Auriemma, C. De Rosa, R. Di Girolamo, A. Silvestre, A.M. Anderson-Wile, G.W. Coates, Small angle x-ray scattering investigation of norbornene-terminated syndiotactic polypropylene and corresponding comb-like poly (macromonomer), J. Phys. Chem. B. 117 (2013) 10320–10333.
- [53] B. Wunderlich, Molecular nucleation and segregation, Faraday Discuss. Chem. Soc. 68 (1979) 239–243.
- [54] B. Wunderlich, A. Mehta, Macromolecular nucleation, J. Polym. Sci. Polym. Phys. Ed. 12 (1974) 255–263.

# **Chapter 3**

# Heterogeneous bubble nucleation by homogeneous crystal nuclei in poly (Llactic acid) foaming<sup>2</sup>

# **3.1 Introduction**

Production of plastics is increasing day by day [1] and recently the theme of plastic pollution is attracting a great research interest. Bio-based plastics are becoming increasingly important in industry as environmentally benign substitutes of plastics derived from fossil resources [2].

Poly (L-lactic acid) (PLLA) is an environmental friendly thermoplastic polyester [3]. It is bio-based and its production from biomasses releases a lower amount of carbon dioxide with respect to the production of oil-based plastics [4]. PLLA can biodegrade in nature to carbon dioxide, water, and humus-like matter [5–7] and in the human body to the natural metabolite l-lactic acid, thanks to the ester groups in its chain that make the polymer susceptible to enzymatic attack [8]. Being also biocompatible, PLLA finds applications in tissue engineering and biomedicine as medical implants [9]. Besides medical applications, PLLA is used in a variety of industrial fields, which mainly include food packaging [10], agriculture, thermal and sound insulation in construction [11], reflectors in LED lamps [12], 3D printing, in bulk or foamed form [2]. In particular, PLLA foam use is expected to grow in the near future, as promising substitute to oil-based plastics foams (e.g., polystyrene foams) [13][14]. PLLA foams are most commonly produced using  $CO_2$  as a physical blowing agent [9,15] with a wide range of applications related to their versatility in terms of foam densities and cell

<sup>&</sup>lt;sup>2</sup> The work presented in this chapter has been published as: Longo A., Di Maio E., Di Lorenzo M.L, 2022. Heterogeneous bubble nucleation by homogeneous crystal nuclei in poly (L-lactic acid) foaming. Macromolecular Chemistry and Physics 2100428. DOI: https://doi.org/10.1002/macp.202100428

morphologies, and the corresponding vast scenario of structural and functional properties has been well documented in the scientific and technical literature [13,15–18].

Designing cell morphology of the foams in terms of cell number density, dimension and other features like open/closed character, wall/strut ratio and anisotropy, has been proven effective in tuning both the functional and structural properties. Numerous strategies are available to control the processes of nucleation, growth and stabilization of foam bubbles that lead to the final cell morphology. In particular, the initial formation of bubbles, i.e bubble nucleation process, can be enhanced by the use of interfaces which ease their formation by reducing the nucleation energy barrier, as described in the context of classical (heterogeneous) nucleation theory [19,20].

Polymer compounding of PLLA with different natural and synthetic additives [21–23] and blending with other polymers have been reported as effective ways to exploit the heterogeneous bubble nucleation mechanism [15]. Presence of additives facilitates the heterogeneous nucleation at interfaces, where phase boundaries can act as nucleation sites for bubbles [24]. Incorporation of nucleating agents such as halloysite [25], microfibrillated cellulose [26], talc [27], modified silica nanoparticles [28], or hydroxyl functionalized graphene [29], have been proven effective on foaming, by reducing cells average diameter and enhancing cell number density. Unfortunately, the addition of fillers or other components to PLLA also alters the purity of the polymer, making recycling and biodegradation of the material more difficult, and may also influence its biocompatibility.

External additives (of different nature) are not the only entities which may act as heterogeneous nucleation sites. In fact, in semi-crystalline polymers, the interface between crystal and amorphous phase (of the same, neat polymer) has been proved effective as nucleating agent [15]. Numerous experimental papers addressed this issue and quantitative data correlate the number and size of cells with spherulite density and surface area [30,31] along with the modeling papers interpreting the role of the crystal/amorphous interphase. Despite the promotion of bubble nucleation, the presence of crystals along all the foaming stages may also be detrimental, sometimes preventing a fine tuning of the foam structure. In fact, crystal formation not only enhances bubble nucleation, but leads also to a decrease of the average CO<sub>2</sub> amount in the system, as CO<sub>2</sub> can be dissolved only in the amorphous areas. This in turn leads to a reduction of the fraction of sample that can undergo bubble formation, thus limiting expansion [32]. Furthermore, crystals act as physical crosslinks among the macromolecules, soon (i.e. at few percent crystalline fraction) inducing a viscosity increase which is unsuitable for the bubble growth. In other words, despite the favorable effect on bubble nucleation, crystal formation on foaming is mostly avoided, also considering the difficulty in controlling the crystalline fraction that may evolve rapidly at foaming processing conditions. In this context, it is worth of note the important effect of strain and of its rate on the crystallization, which is known as flow-induced crystallization (FIC). FIC is particularly effective in extensional (rather than shear) deformation regimes, which are in fact the ones exerted by the polymer between two

growing bubbles. As a semi-crystalline polymer, foaming of PLLA requires a careful selection of processing variables, to cope with the negligible blowing agent solubility in the crystal phase, the divergent viscosity of the system during crystallization, and the interaction and mutual nucleating effect of crystals and bubbles [30,33,34], not an easy, reproducible and industrially scalable task.

Despite the above difficulties in foaming semi-crystalline polymers, in this manuscript we propose a novel procedure to exploit some features of polymer crystallization that may allow attaining foams with tailored morphology, avoiding at the same time, sizable crystal formation before foaming. Similar to foaming, polymer crystallization proceeds via crystal nucleation and growth [35,36]. Nucleation can be heterogeneous, when crystals grow upon external surfaces, cavities, or cracks of insoluble particles, or homogeneous, when few parallel polymer chain segments, called homogeneous crystal nuclei (HCN) aggregate and reach a supercritical size that is sufficiently stable to initiate crystal growth on their surface [35,36]. Compared to heterogeneous nucleation, the density of HCN is about 10<sup>9</sup> times larger [37], and crystals grown from HCN may be so small to grow not to the typical lamellar/spherulitic shape, but to a nodular morphology of nanometer size [38].

One important feature of homogeneous crystal nucleation is that HCN can grow to supercritical size at temperatures where crystal growth rate is negligible [39], which implies that a proper choice of experimental conditions can allow to develop structures that can favor bubbles growth, without measurable formation of crystals [40].

The kinetics of formation of HCN has been recently investigated for PLLA, and detailed knowledge of the effect of molar mass, chain structure on their development kinetics and thermal stability is now available [41–44][45]. Based on these literature information, we have explored the feasibility of HCN as nucleation sites for bubble growth in PLLA foams, with preliminary results detailed in this manuscript. Since HCN may promote growth of both crystals and bubbles, and since  $CO_2$  largely enhances crystal growth rate, care must be taken to tailor processing conditions, in order to limit crystal growth before expansion, as discussed below. PLLA was chosen to test this novel foaming route, but the present approach may be applied also to other foamable semi-crystalline polymers.

# **3.2 Materials and Methods**

### Materials

A commercial PLLA grade with 1-isomer content of 96% and melt-flow index of 6 g  $\cdot$  (10 min)<sup>-1</sup> (210°C/2.16 kg), grade name PLA Lx175 [46] was kindly provided by Total Corbion (The Netherlands). Before processing, PLLA was dried in an oven at 60°C under vacuum overnight. To have a uniform sample size, PLLA pellets were compression molded with a Carver Laboratory Press at a temperature of 190°C for 2 min, without any applied pressure, to allow complete melting. After this period, a pressure of about 20 bar was applied for 2 min. Successively, the press plates equipped with cooling coils were cooled to room temperature. Slabs with thickness of 0.5 mm were obtained, which were then cut into disks of a diameter of 5 mm with a hollow punch.

### **Sample Preparation**

A Perkin-Elmer Pyris Diamond DSC, equipped with an Intracooler II cooling system that allows cooling rates high enough to attain a fully amorphous PLLA and ensures an optimal temperature control and the reproducibility of the nucleation process was used to prepare samples with different HCN density, as well as for the subsequent crystal growth.

The instrument was calibrated in temperature and energy with a high purity indium standard, dry nitrogen at a rate of 30 ml $\cdot$ min<sup>-1</sup> was used as purge gas.

Samples were melted at 200°C for 3 minutes, followed by rapid cooling to 0°C at a rate of 100 K·min<sup>-1</sup> to attain amorphous PLLA. Literature data indicate that cooling at this rate to below  $T_g$  can prevent nuclei formation in a PLLA grade of  $M_w = 120$  kDa and containing 4 % d-isomer [43]. Based on the procedure reported in Ref. [41], after cooling to 0°C, the samples were heated to 60°C at a rate of 100 K·min<sup>-1</sup> and annealed for various nucleation times,  $t_n = 0.5$ , 2 and 4 hours.

#### Thermal analysis

The power-compensated DSC, described above, were used for thermal analysis of foamed and un-foamed samples.

The efficiency of nuclei formation was evaluated using Tammann's two stage crystal nuclei development method, which consists in evaluating HCN formation after their growth to crystals at higher temperature [47,48]. Specifically, after nucleation at 60°C for various  $t_n$ , the samples were heated at 100 K·min<sup>-1</sup> to 120°C and allowed to crystallize at 120°C for 3 min, then rapidly cooled to 0°C at a rate of 100 K·min<sup>-1</sup> to prevent additional formation of crystals.

Thermal properties of the samples, before and after foaming, were analyzed upon heating at  $20 \text{ K} \cdot \text{min}^{-1}$ . To gain precise heat capacity data from the heat flow rate measurements, each scan was accompanied by a reference empty pan run. Each measurement was repeated three times to ensure reproducibility.

#### **Preparation of PLLA foams**

Foaming was conducted in a batch autoclave named "minibatch" extensively described in [49] using  $CO_2$  as blowing agent (SOL Group, Italy). The autoclave consists in a chamber with approximate volume of 1 cm<sup>3</sup>, equipped with a Pt100 temperature sensor (TR1M, GEFRAN) to control the temperature by a PID controller (Ascon. New England temperature solutions, Attleboro, MA, X1), a gas dosing port connected to a syringe pump 500D (Teledyne Isco, Lincoln, NE) and a pressure transducer (F031047, GEFRAN) used to measure the pressure. The pressure release system consists of a pneumatic electrovalve (TSR-20, TruTorq Actuators), designed to ensure a fast depressurization rate of the order of 10 MPa·s<sup>-1</sup>. Samples were charged by a port equipped with a quick connection to allow fast sample removal operations.

Autoclave temperature was set to 120°C and the sample was placed in the chamber after preset temperature was reached, to limit crystallization before foaming. CO<sub>2</sub> was injected into the autoclave to reach a pressure of 10 MPa. Samples were saturated for 3 minutes, then the pressure was released to atmospheric pressure (0.1 MPa) at a rate of 50 MPa·s<sup>-1</sup> to obtain foamed samples. Considering the available diffusivity data of PLLA/CO<sub>2</sub> system [15], 3 minutes can be considered sufficient to attain a uniform CO<sub>2</sub> concentration within the 0.5 mm thick slab, since the characteristic diffusion time ( $\tau_D$ ) is:

$$\tau_D = \frac{(0.5/2 \ mm)^2}{D_{CO_2 - PLLA}} \sim 10^2 s \tag{1}$$

where  $D_{CO_2 - PLLA} = 6 \cdot 10^{-3} mm^2 \cdot s^{-1}$ .

The thermal and pressure protocol used for PLLA foaming is sketched in Figure 3.1. Sample codes are reported in Table 3.1, where samples analyzed before foaming are identified by a "B" and the foamed formulations are identified by an "F", and followed by number referring to  $t_n$ .



Figure 3.6. Scheme of the employed thermal and pressure protocol for PLLA foaming.

1		
Sample	$t_n$ (h)	Foaming
B-0	0	No
B-0.5	0.5	No
B-2	2	No
B-4	4	No
F-0	0	Yes
F-0.5	0.5	Yes
F-2	2	Yes
F-4	4	Yes

Гable	3.1.	Sample	codes
-------	------	--------	-------

# Scanning electron microscopy

Foam morphology was evaluated using a FEI Quanta 200 FEG Scanning Electron Microscope. Before analysis the foams were blade cut and double sputtered/coated with an Au-Pd alloy using a Baltech Med 020 Sputter Coater System, then mounted on aluminum stubs.

The number density of nucleated cells,  $N_0$ , was calculated by [50]:

$$N_0 = \binom{n}{A}^{3/2} \varphi \tag{2}$$

where *n* is the number of cells counted in *A*, the area of micrograph and  $\varphi$  is expansion ratio calculated as:

$$\varphi = \frac{\rho_{Bulk}}{\rho_{Foam}} \tag{3}$$

where  $\rho_{Bulk}$  and  $\rho_{Foam}$  are bulk densities of neat PLLA and of foamed sample (in g·cm<sup>-3</sup>) respectively measured according to ASTM-D1622-03.

# X-ray Diffraction (XRD)

X-ray diffraction spectra were collected with a PANalytical X'PertPro diffractometer equipped with a PIXCel 1D detector, under CuK $\alpha$  radiation. Sample spectra were collected in the range 5-40° 2 $\theta$ , with a step size of 0.013° 2 $\theta$  and counting time of 20 s per step.

# **Optical Microscopy**

A Zeiss Axioskop Polarized Optical Microscope (POM) equipped with a Linkam THMS 600 hot stage and a Scion Corporation CFW-1312C Digital Camera was used to quantify crystal nucleation. Images were captured with Image-Pro Plus 7.0 software (Media Cybernetics). A thin film of PLLA was obtained by squeezing samples between two glass slips on a hot plate, and then thermal treated using the same thermal protocol detailed before: amorphous PLLA was annealed at 60°C for various  $t_n$ , then heated to 120°C for 3 min in a hot stage. At the end of the crystallization step, samples were quenched in liquid nitrogen to stop further crystal growth. Nitrogen gas was fluxed in the hot stage during thermal treatment to prevent degradation. The optical micrographs were used to evaluate the spherulite number density ( $S_0$ ) per unit area, evaluated upon an area of ~ 1.10<sup>-3</sup> cm<sup>2</sup>.

# 3.3 Results and discussion

Literature data on nucleation kinetics of PLLA indicate that, for a grade with melt flow index  $6 \text{ g} \cdot (10 \text{ min})^{-1} (210^{\circ}\text{C}/2.16 \text{ kg})$  and containing 4 % of d-isomer, i.e. with similar molar mass and stereoregularity of the polymer used here, the onset time of crystal nucleation is around 0.3 h at 60°C [43]. Based on this piece of information, three different  $t_n$  were selected, from 0.5 to 4 h, and the efficiency of crystal nucleation was quantified using Tamman's method [47,48], with samples maintained at 120°C for 3 min to allow spherulite growth after HCN formation.

The apparent specific heat capacity data ( $c_p$ ) of PLLA annealed at 60°C for various  $t_n$  then crystallized at 120°C is presented in Figure 3.2. Sample B-0, i.e. the polymer quenched from the melt to below  $T_g$  and immediately reheated to 120°C, displays a step-like increase of the heat capacity at 60°C due to glass transition and, on further heating, a small endotherm centered around 160°C revealing melting of crystals grown at 120°C. Annealing at 60°C before crystallization at 120°C leads to an increase of the area of the melting peak, which becomes more pronounced with the increase of  $t_n$  (samples B-0.5, B-2, B-4). This is due to an increased fraction of crystals grown at 120°C within the pre-defined crystallization time of 3 min, and is paralleled by a progressive decrease of the heat-capacity step at  $T_g$ , due to the lower amorphous fraction.



**Figure 3.7.** Apparent heat capacity (*c*<sub>p</sub>) of PLLA after annealing at 60°C, followed by isothermal crystallization at 120°C, measured upon heating at 20 K ⋅ min<sup>-1</sup>.

Integration of the endothermic peaks and comparison with enthalpy of melting of 100% crystalline PLLA [51] yields the crystal fraction ( $X_c$ ), with data reported in Table 3.2. Crystallinity

of PLLA sizably increases with  $t_n$ , from  $X_C = 0.07$  for B-0 to  $X_C = 0.28$  for B-4. These data indicate that progressive increase of  $t_n$  leads to a corresponding increase of the density of HCN, which in turn favors growth of a larger number of spherulites, and results in a higher  $X_C$ , in line with literature data [41–43,52,53].

Sample	$X_C$
B-0	0.07
B-0.5	0.14
B-2	0.21
B-4	0.28

**Table 3.2**  $X_C$  of PLLA developed after annealing at 60°C for  $t_n$ , followed by isothermal crystallization at 120°C for 3 min.

The variation of the density of crystal nuclei caused by the different  $t_n$  was confirmed by polarized optical microscopy (POM). Since HCN are not visible with POM, Tamman's two-stage nuclei method has been exploited also in this analysis. The optical micrographs shown in Figure 3.3, illustrate the influence of  $t_n$  on PLLA morphology.



**Figure 3.8.** POM micrographs of PLLA cold crystallized at 120°C for 3 min after aging at 60°C for various  $t_n$ : a) B-0; b) B-0.5; c) B-2; d) B-4.

The optical micrographs of Figure 3.3 display, for all samples, PLLA spherulites with about 6.5 μm diameter developed after 3 min of isothermal crystallization at 120°C. Moreover, the

spherulites number density ( $S_0$ ) increases with  $t_n$ . This increase is quantified in Figure 3.4, which displays  $S_0$  as function of  $t_n$ . On the same plot, the variation of  $X_C$  with  $t_n$  (data retrieved from Table 3.2), is also shown for comparison.  $S_0$  progressively increases of about one order of magnitude from B-0 to B-4, and is paralleled by a corresponding increase of  $X_C$  for samples subjected to the same thermal history, which in turn is linked to the higher number of crystals growing on HCN. In other words, POM analysis, in line with DSC data, confirm that the chosen experimental conditions lead to a sizably varied number density of HCN with increasing  $t_n$  at 60°C, in agreement with literature data [36].



**Figure 3.4.**  $S_0$  (black circles) as a function of  $t_n$  at 60°C, determined from optical micrographs of Figure 3.3, compared with  $X_C$  (red squares) measured by DSC plots of Figure 3.2.

In foaming experiments, PLLA samples annealed for various  $t_n$  at 60°C were utilized. In this case, the crystallization was conducted in the autoclave under CO<sub>2</sub> pressure at 10 MPa, 120°C for 3 minutes. The resulting foamed samples, F-0 to F-4 were analyzed in terms of cellular morphology and expansion ratio. The cellular morphology of obtained foams is illustrated in Figure 3.5. F-0 and F-0.5 display a uniform morphology, with only some slight reduction in bubble size of sample nucleated for 0.5 h before foaming. When PLLA is maintained for longer time at 60°C, the foam morphology becomes bimodal, with the formation of two types of cells, as seen in Figures 3.5-C and 3.5-D: large bubbles developed in the bulk, and much smaller cells grown in a "stamen-like cell structure", where round entities corresponding to PLLA spherulites appear surrounded by several elongated cells [54]. This morphology reveals heterogeneous nucleation of cells on a bubble nucleating site, which in this case is the spherulite [54]. The spherulites were grown before foaming,

during the sorption step. Looking at Figure 3.4, which reports the optical micrographs of PLLA spherulites grown at 120°C for 3 min in N<sub>2</sub> at atmospheric pressure after homogeneous crystal nucleation at 60°C, a  $t_n = 0.5$  h leads to only a minor increase of crystal nucleation density, which rationalizes the similar morphology of the foams displayed in Figures 3.5-a and 3.5-b. Conversely, a marked increase of crystal nucleation density is revealed after annealing PLLA at 60°C for longer times,  $t_n \ge 2$  h: these HCN grow to small spherulites during the 3-minute sorption of CO<sub>2</sub>, and act as solid substrate/interface for bubble growth. The average diameter of the spherulites seen in Figure 3.5 is around 20  $\pm$  10  $\mu$ m, only slighter larger than the same spherulites grown at the same temperature for the same time under N<sub>2</sub> at atmospheric pressure (see Figure 3), whose diameter is 6.5  $\mu$ m, as reported above. The somewhat higher size of the spherulites seen in Figure 3.5 is to be linked to the faster spherulite growth rate of PLLA in the presence of CO<sub>2</sub>, which plasticizes the polymer, as well documented in the literature [55–57].



**Figure 3.5.** SEM micrographs of PLLA foamed after annealing at 60°C for *t<sub>n</sub>* ranging from 0 to 4 h, followed by 3-minute sorption of CO<sub>2</sub> at 10 MPa and 120°C: a) F-0; b) F-0.5; c) F-2; d) F-4.

The electron micrographs of Figure 3.5 were used to calculate the average cell size, measured averaging the larger and smaller diameters of elongated bubble, and number density of nucleated cells,  $N_0$ , reported in Figure 3.6. The patterned data points reveal the overall increase of  $N_0$  with  $t_n$ ,

whereas the close and open data points distinguish cells grown in the bulk and in the stamen-like regions, respectively. On the same plot, the average cell size data are also presented, again with open and close symbols for samples that display a bimodal morphology and hatched data referring to the average value. Increasing  $t_n$  leads to an overall increase of bubble number, whose average size also progressively decreases with  $t_n$ . Sample F-4, foamed after HCN development for 4 h at 60°C, displays the largest  $N_0$  (1.1 · 10<sup>7</sup> cells · cm<sup>-3</sup>) and the smallest cell size both in the bulk and in the stamen-like regions, with a decrease of bubble size of 2 orders of magnitude in the stamen-like regions, compared to F-0.



Figure 3.6  $N_0$  (black circles) and cell size (red squares) of foams as a function of  $t_n$ . The close and open symbols refer to bulk and stamen regions, respectively, the hatched data are the total  $N_0$  and average values for cell size.

Data of expansion ratio ( $\varphi$ ), i.e. the ratio between density of bulk and foamed PLLA (eq. 3), are presented in Table 3.3. A non-monotonic variation of  $\varphi$  is evident from the data, as sample F-0.5 displays a remarkable gain in expansion ratio compared to F-0, with  $\varphi$  that decreases in PLLA foamed after longer  $t_n$ .

Sample	arphi
F-0	7.75
F-0.5	24.8
F-2	15.5
F-4	20.7

Table 3.3. Expansion ratio of PLLA foams

Additional information on the effect of annealing at 60°C before foaming is revealed by comparison of the volume fraction of the cells, estimated from SEM micrographs, with degree of expansion. Having determined  $N_0$  both in bulk ( $N_{0Bulk}$ ) and stamen-like ( $N_{0Stamen}$ ) areas, and having measured the corresponding representative cell diameter ( $Size_{Bulk}$  and  $Size_{Stamen}$ ), it is possible to estimate the total void volume ( $V_V$ ) by combining the volume of the two different type of cells ( $v_{Bulk}$ and  $v_{Stamen}$ ). By normalizing  $V_V$ , one may infer about the contribution to expansion by large and small cells to justify non-monotonic effect of  $t_n$  on  $\varphi$ .

Partial *v* values of bulk ( $v_{Bulk}$ ) and stamen ( $v_{Stamen}$ ) cells are presented in Figure 3.7 as function of  $t_n$ . On the same plot, the expansion ratio data, taken from Table 3.3 are also shown. Both  $v_{Bulk}$  and  $\varphi$  display similar non-monotonic trend with  $t_n$ , with a much higher volume and larger expansion attained when PLLA is foamed after annealing at 60°C for 0.5 h. It is also clearly visible how small stamen cells contribute in a small way to  $V_V$  and therefore to expansion, possibly justifying the reduced expansion at larger  $t_n$ .

To further rationalize the large expansion and volume of sample F-0.5, crystallization kinetics of PLLA needs to be taken into account. As shown in Figure 3.2, annealing PLLA at 60°C for 0.5 h before crystal growth at 120°C, leads to an only minor increase in  $X_C$ , whereas sizable increase in crystallinity takes place when the polymer is annealed at 60°C for longer  $t_n$ . By recalling that the crystalline phase is impermeable to the blowing agent, in samples with low  $X_C$  only a minor reduction of CO<sub>2</sub> sorption takes place when the polymer is placed within the foaming reactor at 120°C under CO<sub>2</sub> at 10 MPa. Conversely, in samples with larger  $X_C$ , the amount of blowing agent is reduced.

It is worth to remember to the reader that data shown in Figure 3.2 were measured under  $N_2$  flow at atmospheric pressure which has negligible effect on crystallization kinetics with respect to the plasticization due to CO<sub>2</sub> [56]. This makes the comparison between  $X_C$  gained during DSC or microscopy analysis and during the overall foaming process only qualitative.



Fig 3.7.  $v_{Bulk}$  (filled circles),  $v_{Stamen}$  (empty circles) and  $\varphi$  (squares) as functions of  $t_n$ 

To complete details of the feasibility of the proposed method, thermal and structural analysis of PLLA foams are presented in Figures 3.8 and 3.9. Figure 3.8 illustrates the heat capacity plots of PLLA foams, whose morphology is illustrated in Figure 3.5. The various foams display only minor differences in thermal output, all having a  $X_C$  around 0.34, slightly higher when compared with B-4 ( $X_C = 0.28$ ). Despite the varied initial crystallinity before foaming, flow-induced crystallization (FIC) occurs upon bubble development, and results in a comparable development of crystal fraction in all the analyzed samples. It is worth to note that the polymer further crystallizes upon DSC heating for all samples, as revealed by the cold crystallization exotherm centered around 110°C, well visible for all samples.



**Figure 3.8.** Apparent specific heat capacity  $(c_p)$  of PLLA foams, measured upon heating at 20 K · min<sup>-1</sup>.

X-ray diffraction analysis of the foams is exampled in Figure 3.9 for sample F-4, being similar to X-ray diffraction patterns of the other foamed samples. The diffraction pattern shown in Figure 3.9 is typical of  $\alpha$ -crystal modification of PLLA: the spectrum presents main diffraction peaks at  $2\theta = 16.5$  and 19 °, plus a reflection at 22.2 °, which is observed only in PLLA containing  $\alpha$ -crystals, and the reflection at 24.5 ° characteristic of  $\alpha$ '-crystals is absent [58,59]. The X-ray profile of Figure 3.9 is in agreement with literature data, which indicate that foaming of semi-crystalline PLLA leads to growth of  $\alpha$ -crystals, even in the presence of nucleating sites [60,61], proving the proposed strategy of foaming PLLA in the presence of HCN does not affect structural properties of PLLA foams.



Figure 3.9. X-ray diffraction pattern of PLLA foamed after annealing at 60°C for  $t_n = 4$  (sample F-4).

# **3.4 Conclusions**

PLLA slabs with a thickness of 0.5 mm were homogeneously nucleated by annealing at  $T_g$  for a  $t_n$  varying from 0.5 to 4 h. The increase in  $t_n$  results in an increased spherulites number density  $S_0$ , grown on homogeneous nuclei. Nucleated samples were physical foamed at 120°C and 10 MPa of CO<sub>2</sub> with a sorption time of 3 minutes. The foams display minor differences in thermal properties, all having a  $X_C$  around 0.34 and the same  $\alpha$ -crystals form of the neat polymer.

The morphology of the foams was observed with SEM and the increasing in  $t_n$  leads to a monotone decrease in cell size and larger bubble density. A nucleation for  $t_n$  0.5 results in a minor increase on the cell nucleation density on the surface of HCN, while samples with  $t_n$  2 and 4 h, show a bi-modal morphology with the formation of two different types of cells, bigger in the bulk and smaller stamen-like cells surrounding growing spherulites. The expansion ratio ranged from 7.75 to 24.8 with the maximum value for the sample nucleated for  $t_n = 0.5$  h. This is rationalized with the presence of HCN in sample with  $t_n = 0.5$  h leads to a minor increase in  $X_C$ . Conversely, samples with  $t_n \ge 2$  show the nucleation of cells on the surface of growing spherulites, resulting in a higher crystallinity and, therefore, in a reduced amount of blowing agent.

The enhancement in foam expansion ratio and morphology due to the presence of homogeneous crystal nuclei, corroborate the advantages of this method to improve foaming of PLLA, avoiding the addition of heterogeneous additives, thereby preserving its biodegradability and biocompatibility.

#### Acknowledgements

The authors warmly thank Ms. Maria Cristina Del Barone of IPCB-CNR and Prof. Paolo Aprea of DICMaPI-UniNa for their assistance with SEM and X-ray diffraction analyses, respectively.
### **3.5 References**

- S.B. Borrelle, J. Ringma, K.L. Law, C.C. Monnahan, L. Lebreton, A. McGivern, E. Murphy, J. Jambeck, G.H. Leonard, M.A. Hilleary, M. Eriksen, H.P. Possingham, H. De Frond, L.R. Gerber, B. Polidoro, A. Tahir, M. Bernard, N. Mallos, M. Barnes, C.M. Rochman, Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution, Science (80-. ). 369 (2020) 1515–1518. https://doi.org/10.1126/science.aba3656.
- B. Gupta, N. Revagade, J. Hilborn, Poly(lactic acid) fiber: An overview, Prog. Polym. Sci. (2007). https://doi.org/10.1016/j.progpolymsci.2007.01.005.
- [3] M.L. Di Lorenzo, R. Androsch, Industrial Applications of Poly (lactic acid), 2018.
- [4] R.N. Darie-Niţə, C. Vasile, A. Irimia, R. Lipşa, M. Râpə, Evaluation of some eco-friendly plasticizers for PLA films processing, J. Appl. Polym. Sci. (2016).
  https://doi.org/10.1002/app.43223.
- [5] R. Gattin, A. Copinet, C. Bertrand, Y. Couturier, Biodegradation study of a coextruded starch and poly(lactic acid) material in various media, J. Appl. Polym. Sci. (2003). https://doi.org/10.1002/app.11701.
- [6] M.L. Di Lorenzo, R. Androsch, Synthesis, Structure and Properties of Poly(lactic acid), Springer, 2018. https://doi.org/10.1007/978-3-319-64230-7.
- [7] R.E. Drumright, P.R. Gruber, D.E. Henton, Polylactic acid technology, Adv. Mater. (2000). https://doi.org/10.1002/1521-4095(200012)12:23<1841::AID-ADMA1841>3.0.CO;2-E.
- [8] D. Zhang, M.A. Kandadai, J. Cech, S. Roth, S.A. Curran, Poly(L-lactide) (PLLA)/Multiwalled Carbon Nanotube (MWCNT) Composite: Characterization and Biocompatibility Evaluation, J. Phys. Chem. B. 110 (2006) 12910–12915. https://doi.org/10.1021/jp061628k.
- [9] P. Netti, Biomedical foams for tissue engineering applications, (2014).
- [10] L. Wang, R.E. Lee, G. Wang, R.K.M.M. Chu, J. Zhao, C.B. Park, Use of stereocomplex crystallites for fully-biobased microcellular low-density poly(lactic acid) foams for green packaging, Chem. Eng. J. 327 (2017) 1151–1162.
  https://doi.org/https://doi.org/10.1016/j.cej.2017.07.024.
- [11] J.M. Julien, J.C. Quantin, J.C. Bénézet, A. Bergeret, M.F. Lacrampe, P. Krawczak, Chemical foaming extrusion of poly(lactic acid) with chain-extenders: Physical and morphological characterizations, Eur. Polym. J. 67 (2015) 40–49.

https://doi.org/10.1016/j.eurpolymj.2015.03.011.

- [12] C.C. Kuo, L.C. Liu, W.C. Liang, H.C. Liu, C.M. Chen, Preparation of polylactic acid (PLA) foams with supercritical carbon dioxide and their applications for reflectors of white light-emitting diode (LED) lamps, Mater. Res. Bull. 67 (2015) 170–175. https://doi.org/10.1016/j.materresbull.2015.03.026.
- [13] K. Parker, J.P. Garancher, S. Shah, S. Weal, A. Fernyhough, Polylactic Acid (PLA) Foams for Packaging Applications, in: Handb. Bioplastics Biocomposites Eng. Appl., 2011. https://doi.org/10.1002/9781118203699.ch6.
- [14] K. Parker, J.P. Garancher, S. Shah, A. Fernyhough, Expanded polylactic acid An ecofriendly alternative to polystyrene foam, J. Cell. Plast. 47 (2011) 233–243. https://doi.org/10.1177/0021955X11404833.
- [15] M. Nofar, C.B. Park, Poly (lactic acid) foaming, Prog. Polym. Sci. 39 (2014) 1721–1741. https://doi.org/10.1016/j.progpolymsci.2014.04.001.
- [16] S.G. Mosanenzadeh, H.E. Naguib, C.B. Park, N. Atalla, Development, characterization, and modeling of environmentally friendly open-cell acoustic foams, Polym. Eng. Sci. 53 (2013) 1979–1989.
- [17] M. Ajioka, K. Enomoto, A. Yamaguchi, K. Suzuki, T. Watanabe, Y. Kitahara, Degradable foam and use of same, (1995).
- P. Tiwary, C.B. Park, M. Kontopoulou, Transition from microcellular to nanocellular PLA foams by controlling viscosity, branching and crystallization, Eur. Polym. J. 91 (2017) 283–296. https://doi.org/10.1016/j.eurpolymj.2017.04.010.
- [19] S.N. Leung, A. Wong, L.C. Wang, C.B. Park, Mechanism of extensional stress-induced cell formation in polymeric foaming processes with the presence of nucleating agents, J. Supercrit. Fluids. 63 (2012) 187–198.

https://doi.org/https://doi.org/10.1016/j.supflu.2011.12.018.

- [20] C. Wang, S.N. Leung, M. Bussmann, W.T. Zhai, C.B. Park, Numerical Investigation of Nucleating-Agent-Enhanced Heterogeneous Nucleation, Ind. Eng. Chem. Res. 49 (2010) 12783–12792. https://doi.org/10.1021/ie1017207.
- M. Mihai, M.A. Huneault, B.D. Favis, H. Li, Extrusion foaming of semi-crystalline PLA and PLA/thermoplastic starch blends, Macromol. Biosci. 7 (2007) 907–920. https://doi.org/10.1002/mabi.200700080.

- [22] Y. Wu, X. Zhou, J. Li, K. Yu, L. Wang, J. Ma, Mechanism of Heterogeneous Bubble Nucleation in Polymer Blend Foaming, J. Phys. Chem. B. 125 (2021) 6709–6716. https://doi.org/10.1021/acs.jpcb.1c03087.
- [23] J. Zhang, X. Sun, Biodegradable foams of poly (lactic acid)/starch. I. Extrusion condition and cellular size distribution, J. Appl. Polym. Sci. 106 (2007) 857–862.
- [24] J.A. Sarver, E. Kiran, Foaming of polymers with carbon dioxide The year-in-review 2019,J. Supercrit. Fluids. 173 (2021) 105166.

https://doi.org/https://doi.org/10.1016/j.supflu.2021.105166.

- [25] B. Morlin, K. Litauszki, R. Petrény, Á. Kmetty, L. Mészáros, Characterization of polylactic acid-based nanocomposite foams with supercritical CO<sub>2</sub>, Measurement. 178 (2021) 109385.
- [26] C.I.R. Boissard, P.-E. Bourban, C.J.G. Plummer, R.C. Neagu, J.-A.E. Månson, Cellular biocomposites from polylactide and microfibrillated cellulose, J. Cell. Plast. 48 (2012) 445– 458. https://doi.org/10.1177/0021955X12448190.
- [27] A. Ameli, D. Jahani, M. Nofar, P.U. Jung, C.B. Park, Processing and characterization of solid and foamed injection-molded polylactide with talc, J. Cell. Plast. 49 (2013) 351–374.
- [28] E.J. Jeong, C.K. Park, S.H. Kim, Fabrication of microcellular polylactide/modified silica nanocomposite foams, J. Appl. Polym. Sci. 137 (2020) 48616.
- [29] X. Wang, J. Mi, H. Zhou, X. Wang, Transition from microcellular to nanocellular chain extended poly(lactic acid)/hydroxyl-functionalized graphene foams by supercritical CO<sub>2</sub>, J. Mater. Sci. 54 (2019) 3863–3877. https://doi.org/10.1007/s10853-018-3120-8.
- [30] K. Taki, D. Kitano, M. Ohshima, Effect of growing crystalline phase on bubble nucleation in poly(L-lactide)/CO<sub>2</sub> batch foaming, Ind. Eng. Chem. Res. 50 (2011) 3247–3252. https://doi.org/10.1021/ie101637f.
- [31] Q. Ren, J. Wang, W. Zhai, S. Su, Solid state foaming of poly(lactic acid) blown with compressed CO<sub>2</sub>: Influences of long chain branching and induced crystallization on foam expansion and cell morphology, Ind. Eng. Chem. Res. 52 (2013) 13411–13421. https://doi.org/10.1021/ie402039y.
- [32] X. Zhang, W. Ding, N. Zhao, J. Chen, C.B. Park, Effects of Compressed CO<sub>2</sub> and Cotton Fibers on the Crystallization and Foaming Behaviors of Polylactide, Ind. Eng. Chem. Res. 57 (2018) 2094–2104. https://doi.org/10.1021/acs.iecr.7b04139.
- [33] W. Zhai, Y. Ko, W. Zhu, A. Wong, C.B. Park, A study of the crystallization, melting, and foaming behaviors of polylactic acid in compressed CO<sub>2</sub>, Int. J. Mol. Sci. 10 (2009) 5381–

5397. https://doi.org/10.3390/ijms10125381.

- [34] X. Liao, A.V. Nawaby, P.S. Whitfield, Carbon dioxide-induced crystallization in poly(Llactic acid) and its effect on foam morphologies, Polym. Int. 59 (2010) 1709–1718. https://doi.org/10.1002/pi.2910.
- [35] E. Schulz, B. Wunderlich. Macromolecular physics, vol. 2 crystal nucleation, growth, annealing. Academic Press New York 1976, Wiley Online Library, 1977.
- [36] L. Mandelkern, Crystallization of Polymers: Volume 2, Kinetics and Mechanisms, Cambridge University Press, 2004.
- [37] R. Androsch, A.M. Rhoades, I. Stolte, C. Schick, Density of heterogeneous and homogeneous crystal nuclei in poly (butylene terephthalate), Eur. Polym. J. 66 (2015) 180–189.
- [38] R. Androsch, B. Wunderlich, The link between rigid amorphous fraction and crystal perfection in cold-crystallized poly (ethylene terephthalate), Polymer (Guildf). 46 (2005) 12556–12566.
- [39] R. Androsch, M.L. Di Lorenzo, C. Schick, Kinetics of Nucleation and Growth of Crystals of Poly(L-lactic) acid, in: Synth. Struct. Prop. Poly(Lactic Acid), 2018.
- [40] J.W.P. Schmelzer, A.S. Abyzov, V.M. Fokin, C. Schick, E.D. Zanotto, Crystallization of glass-forming liquids: maxima of nucleation, growth, and overall crystallization rates, J. Non. Cryst. Solids. 429 (2015) 24–32.
- [41] R. Androsch, M.L. Di Lorenzo, Crystal nucleation in glassy poly(L-lactic acid), Macromolecules. (2013). https://doi.org/10.1021/ma401036j.
- [42] R. Androsch, M.L. Di Lorenzo, Kinetics of crystal nucleation of poly (L -lactic acid), Polymer (Guildf). 54 (2013) 6882–6885.
- [43] R. Androsch, M.L. Di Lorenzo, C. Schick, Crystal nucleation in random L/D-lactide copolymers, Eur. Polym. J. (2016). https://doi.org/10.1016/j.eurpolymj.2016.01.020.
- [44] R. Androsch, M.L. Di Lorenzo, C. Schick, Effect of molar mass on enthalpy relaxation and crystal nucleation of poly (L-lactic acid), Eur. Polym. J. 96 (2017) 361–369.
- [45] R.A. Andrianov, R. Androsch, R. Zhang, T.A. Mukhametzyanov, A.S. Abyzov, J.W.P. Schmelzer, C. Schick, Growth and dissolution of crystal nuclei in poly(L-lactic acid) (PLLA) in Tammann's development method, Polymer (Guildf). 196 (2020) 122453. https://doi.org/https://doi.org/10.1016/j.polymer.2020.122453.
- [46] Luminy® PLA neat resins, (n.d.).https://totalcorbion.4net-acc.com/media/iufhvey2/factsheet luminy-pla-neat-

resins\_20190903.pdf.

- [47] G. Tammann, Number of nuclei in supercooled liquids, Z. Phys. Chem. 25 (1898) 441–479.
- [48] G. Tammann, E. Jenckel, Die Kristallisationsgeschwindigkeit und die Kernzahl des Glycerins in Abhängigkeit von der Temperatur, Zeitschrift Für Anorg. Und Allg. Chemie. 193 (1930) 76–80.
- [49] D. Tammaro, V. Contaldi, M.G.P. Carbone, E. Di Maio, S. Iannace, A novel lab-scale batch foaming equipment: The mini-batch, J. Cell. Plast. 52 (2016) 533–543. https://doi.org/10.1177/0021955X15584654.
- [50] K. Yu, J. Ni, H. Zhou, X. Wang, J. Mi, Effects of in-situ crystallization on poly (lactic acid) microcellular foaming: Density functional theory and experiment, Polymer (Guildf). 200 (2020) 122539. https://doi.org/https://doi.org/10.1016/j.polymer.2020.122539.
- [51] M.C. Righetti, M. Gazzano, M.L. Di Lorenzo, R. Androsch, Enthalpy of melting of α'-and αcrystals of poly (L-lactic acid), Eur. Polym. J. 70 (2015) 215–220.
- [52] B. Li, G. Zhao, G. Wang, L. Zhang, J. Hou, J. Gong, A green strategy to regulate cellular structure and crystallization of poly(lactic acid) foams based on pre-isothermal cold crystallization and CO<sub>2</sub> foaming, Int. J. Biol. Macromol. 129 (2019) 171–180. https://doi.org/10.1016/j.ijbiomac.2019.02.026.
- [53] B. Li, G. Zhao, G. Wang, L. Zhang, J. Gong, Fabrication of high-expansion microcellular PLA foams based on pre-isothermal cold crystallization and supercritical CO<sub>2</sub> foaming, Polym. Degrad. Stab. 156 (2018) 75–88.
- [54] L.Q. Xu, H.X. Huang, Foaming of poly(lactic acid) using supercritical carbon dioxide as foaming agent: Influence of crystallinity and spherulite size on cell structure and expansion ratio, Ind. Eng. Chem. Res. 53 (2014) 2277–2286. https://doi.org/10.1021/ie403594t.
- [55] H. Marubayashi, S. Akaishi, S. Akasaka, S. Asai, M. Sumita, Crystalline structure and morphology of poly(L-lactide) Formed under high-pressure CO<sub>2</sub>, Macromolecules. 41 (2008) 9192–9203. https://doi.org/10.1021/ma800766h.
- [56] M. Nofar, A. Tabatabaei, A. Ameli, C.B. Park, Comparison of melting and crystallization behaviors of polylactide under high-pressure CO<sub>2</sub>, N<sub>2</sub>, and He, AIP Conf. Proc. 1593 (2014) 320–323. https://doi.org/10.1063/1.4873791.
- [57] M. Nofar, W. Zhu, C.B. Park, Effect of dissolved CO<sub>2</sub> on the crystallization behavior of linear and branched PLA, Polymer (Guildf). 53 (2012) 3341–3353. https://doi.org/10.1016/j.polymer.2012.04.054.

- [58] M. Dobrzyńska-Mizera, M. Knitter, A. Woźniak-Braszak, M. Baranowski, T. Sterzyński,
  M.L. Di Lorenzo, Poly(L-Lactic Acid)/Pine Wood Bio-Based Composites, Materials (Basel).
  13 (2020). https://doi.org/10.3390/ma13173776.
- [59] M. Cocca, M.L. Di Lorenzo, M. Malinconico, V. Frezza, Influence of crystal polymorphism on mechanical and barrier properties of poly(L-lactic acid), Eur. Polym. J. (2011). https://doi.org/10.1016/j.eurpolymj.2011.02.009.
- [60] S.-J.J. Sheng, X. Hu, F. Wang, Q.-Y.Y. Ma, M.-F.F. Gu, Mechanical and thermal property characterization of poly-L-lactide (PLLA) scaffold developed using pressure-controllable green foaming technology, Mater. Sci. Eng. C. 49 (2015) 612–622. https://doi.org/https://doi.org/10.1016/j.msec.2015.01.025.
- [61] J. Li, X. Liao, Q. Yang, G. Li, Crystals in situ induced by supercritical CO<sub>2</sub> as bubble nucleation sites on spherulitic PLLA foam structure controlling, Ind. Eng. Chem. Res. 56 (2017) 11111–11124.

# **Chapter 4**

# CO<sub>2</sub>-induced mesophase: An easy and green method to tailor crystallization kinetics and morphology in PLLA

# **4.1 Introduction**

Poly (L-lactic) acid (PLLA), as biodegradable polyester, has great potential as substitute to oil-based plastics. The wideness of applications range, which goes from disposable plastics for packaging to foaming for medical engineering [1–6], depends on its biocompatibility and biodegradability, together with macroscopic physical and mechanical properties of the polymer which, in turn, are governed by crystalline structure/morphology parameters [6–9], including crystallinity [10,11] and polymorphism [12–14]. For instance, a specific polymorph improves mechanical and barrier properties [12–14] and a higher degree of crystallinity enhances thermal stability [15,16] but lowers biodegradation ability [7,10,17]. This double effect brings the need in research for an easy way to tune crystalline structure/morphology of the polymer.

As detailed in the previous chapters of this thesis, there are different methodologies to improve PLLA crystallization rates, which include addition of plasticizers [18–20] or compounding the polymer with nucleating additives [18,21,22]. Keeping an eye on recycling and biocompatibility of PLLA, the addition of external agents and the blending with a different material needs to be avoided to keep these fundamental properties of the material unaltered.

Ways to improve the crystallization ability of PLLA with no need to compound with external additives are represented by using transient plasticizers as CO<sub>2</sub> [23–25], modify the chain structure by means of chain extenders [26,27], blending with optical pure, low molecular weight PLLA [28,29], or thermal annealing the polymer at temperatures close to its glass transition temperature

 $(T_g)$ . The latter promotes aggregation of short chain segments, called homogeneous crystal nuclei (HCN), resulting in a much higher crystallization rate upon heating [30–32] as reported in Chapter 3, where HCN have been exploited also as heterogeneous nucleating agents for bubbles in PLLA foaming.

Chapter 2 of this thesis details a successful attempt to enhance crystallization kinetics of a slowly crystallizing commercial PLLA grade, by means of radical branching of short chains made of optically pure, low molecular weight PLLA. The fast crystallizing short branches act as molecular nucleating agents, enhancing crystallization rate of the commercial PLLA, which results in improved thermal properties, keeping, at the same time, the chemical purity of the material unaltered [33].

Even if improving crystallization kinetics of PLLA by means of modification of the chain structure proved to be effective in tailoring the properties of the material, this process has the drawback of not being easily and fast tunable. Each chemical modification produces a material with different thermal properties, which means that, when there is the need of a different crystallization rate, a new reaction with different reagents and parameters is required.

The ideal situation would be a process that helps tuning crystalline structure/morphology of PLLA in a fast and economic way, like sample pre-treatment, or modification of process parameters.

Similar to other thermoplastic polyesters, PLLA displays crystal polymorphism [34,35]. Depending on thermal and mechanical treatments, PLLA can crystallize into three different crystal forms named  $\alpha$ -,  $\beta$ -,  $\gamma$ -. The  $\alpha$ -form is the most stable one, and grows upon melt or cold crystallization, or solvent evaporation, and has two crystal modifications named  $\alpha'$ - and  $\alpha''$ - [13,14]. In addition to these polymorphs, PLLA is also able to co-crystallize with  $CO_2$  [36,37] and some organic solvents [17-19] under specific conditions, to form clathrate structures. When PLLA is exposed to high pressure CO<sub>2</sub> at temperatures below 50 °C, PLLA/CO<sub>2</sub> complex crystals develop [38], where CO<sub>2</sub> molecules are encapsulated in a cavity and surrounded by four PLLA chains in the crystal unit cell [36]. Complete removal of  $CO_2$ , e.g. by degassing at room temperature, leads to the emptied form of PLLA-CO<sub>2</sub> complex, known as  $\alpha''$ -modification [36]. Both PLLA-CO<sub>2</sub> and the emptied form  $\alpha''$ -crystals are disordered and have a looser chain packing compared to the thermally stable  $\alpha$ -crystals [36]. Such disorder allows their easy identification by infrared spectroscopy, as detailed below. Other disordered PLLA mesophase was also reported to develop upon tensile drawing at temperatures around 65-90 °C, as a disorder-order transition directly correlated with a critical strain or orientation of the amorphous chains [39–41]. Mesophase formation can be promoted also by blending or copolymerization [42], but this inevitably leads to some negative aspects such as incompatibility, deterioration of homogeneity and alteration of biocompatibility. PLLA mesophases, either produced by  $CO_2$  exposure or by strain, are metastable and transform to the ordered  $\alpha$ - phase with increasing temperature above 90 °C [42]. It has been demonstrated that mesophase not only accelerates crystallization of PLLA [43,44] upon subsequent heating, but also influences crystal morphology [44,45]. In fact, crystallization attained via  $CO_2$ -induced mesophase may lead to either micro-spherulites or nano-rods, depending on temperature and  $CO_2$  pressure, with transition from micro-spherulites to rod-like nanostructures occurring around 15 °C under 7-15 MPa  $CO_2$  and around 30 °C under 3 MPa  $CO_2$  [46].

Some literature data on the effect of mesophase on the isothermal crystallization behavior and on crystal morphology of PLLA are available [44,45,47], but most studies are limited to formation of CO<sub>2</sub>-induced mesophase at temperatures as low as 0 °C and upon long saturation times, of a few hours at 0 °C. In this chapter, we detail formation of PLLA mesophase at room temperature, after short saturation times of a few minutes, and the effect of the mesophase on thermal properties of PLLA. Structural rearrangements of PLLA chains are induced by keeping an initially amorphous polymer under CO<sub>2</sub> at pressures of 3-6 MPa for various times, and the influence of pressure/time on non-isothermal formation of  $\alpha$ -crystals is investigated.

As discussed and detailed in the previous chapter, chain rearrangements leading to nanosized order domains of a few parallel chain segments can be induced in PLLA by annealing at temperatures around  $T_g$ . These nano-sized order domains, known as HCN, can promote the onset of crystal growth of PLLA, accelerating the overall crystallization kinetics. The influence of HCN of formation of  $\alpha$ '- or  $\alpha$ -crystals of PLLA (depending on crystallization temperature) is actually well detailed in the literature, but to our knowledge no literature data on the influence of prior annealing at  $T_g$  on CO<sub>2</sub>-induced mesophase of PLLA are available, hence preliminary data are also presented in this chapter. Finally, the combined influence of HCN and CO<sub>2</sub>-induced mesophase on development of  $\alpha$ -crystals of PLLA is also analyzed and discussed.

Formation of CO<sub>2</sub>-induced mesophase at room temperature with short saturation time, of only a few minutes, opens up the possibility of producing CO<sub>2</sub>-induced mesophase under conditions affordable with any pressure vessel. This procedure appeals as an economic and fast process to tune mesophase fraction, and thus crystallization kinetics and morphology of PLLA, using a green and clean technology that does not involve external compounds that may alter polymer purity, and in turn biodegradability.

### 4.2 Materials and Methods

#### Materials

A commercial PLLA grade with L-isomer content of 96 % and melt-flow index of 6 g  $\cdot$  (10 min)<sup>-1</sup> (210 °C/2.16 kg), grade name PLA Lx175 [48] was kindly provided by Total Corbion (The Netherlands). Before processing, PLLA was dried in an oven at 60°C under vacuum overnight. To have a uniform sample size, PLLA pellets were compression molded with a Carver Laboratory Press at a temperature of 190°C for 2 min, without any applied pressure, to allow complete melting. After this period, a pressure of about 20 bar was applied for 2 min. Successively, the press plates equipped with cooling coils were cooled to room temperature. Slabs with thickness of 0.5 mm were obtained, which were then cut into disks of a diameter of 5 mm with a hollow punch.

#### Sample preparation and mesophase growth

Samples were thermally treated in a Perkin-Elmer Pyris Diamond DSC, equipped with an Intracooler II cooling system, as in Chapter 3 of the present thesis. Samples were melted at 200°C for 3 minutes, followed by rapid cooling to 0 °C at a rate of 100 K ·min<sup>-1</sup> to attain amorphous PLLA. To obtain samples containing various amounts of homogeneous crystal nuclei, after cooling to 0 °C, the samples were heated to 60°C at a rate of 100 K ·min<sup>-1</sup> and annealed for various nucleation times,  $t_n = 0.5$  and 2 hours.

The mesophase was developed in the batch autoclave named "minibatch" used to prepare foam samples in Chapter 3 of the present thesis and extensively described in [49] and in the "optic foaming" batch autoclave (see Supporting Information for description) using CO<sub>2</sub> as blowing agent (SOL Group, Italy). All the experiments were conducted at room temperature ( $T_{amb}$ ). Samples were placed into the chamber and the CO<sub>2</sub> was injected to reach the desired pressure and samples were saturated. Four different pressures and four different saturation times ( $t_s$ ) have been tested, as reported in Table 4.1.

After saturation with CO<sub>2</sub>, the pressure was released and treated samples were degassed under air atmosphere for one week prior to measurement, to attain  $\alpha''$ -mesophase.

Sample	<i>t<sub>n</sub></i> (h)	$\begin{array}{c} 6 \text{ MPa} \\ t_s \text{ (min)} \end{array}$	$5 \text{ MPa} \\ t_s(\min)$		$\begin{array}{c} 4 \text{ MPa} \\ t_s(\min) \end{array}$		$\begin{array}{c} 3 \text{ MPa} \\ t_s(\min) \end{array}$	
$t_n 0_P_t_s$	0	1	1	3	1	3	1	3
		3	5	20	5	20	5	20
$t_n 0.5 P_t_s$	0.5		1	3	1	3	1	3
			5	20	5	20	5	20
$t_n 2\_P\_t_s$	2		3		3		3	

Table 4.1. Sample code and process parameters

#### Measurements

The presence of mesomorphic chain organization in the samples was tested via FTIR-ATR spectroscopy with a PerkinElmer FTIR Spectrometer Model Spectrum 100 equipped with a PerkinElmer ATR accessory with a diamond crystal. Each spectrum is an average of 16 individual scans and has been recorded with a resolution of 4 cm<sup>-1</sup>.

The power-compensated DSC, described above, was used for thermal analysis of samples. Thermal properties were analyzed upon heating from 0 to 200 °C at 20 K  $\cdot$  min<sup>-1</sup>. Each heat flow rate measurement was repeated three times to ensure reproducibility and the data were analyzed after normalization.

### 4.3 Results and discussions

#### Mesophase formation revealed by FTIR-ATR

After CO<sub>2</sub> treatment, samples were analysed via FTIR-ATR spectroscopy to confirm the presence of mesophase. Crystalline PLLA presents an absorbance band at 922 cm<sup>-1</sup> characteristic of  $\alpha$ - or  $\alpha$ '- form, assigned to the coupling of the CH<sub>3</sub> rocking mode with the C–C backbone stretching, which is sensitive to the 10<sub>3</sub> helix chain conformation [50]. The mesophase influences the infrared spectra in the wavelength range between 950-850 cm<sup>-1</sup>. For strain-induced mesophase, a shift to 918 cm<sup>-1</sup> of this peak has been found [39], and reported also in case of CO<sub>2</sub>-induced mesophase, both emptied and clathrate forms [38,43–45]. Also the band at 870 cm<sup>-1</sup> associated to the vibrational mode of C-COO bond [51] can be used to detect the presence of mesophase, as it shifts to higher wavenumbers with increase in the structural order of the polymer [43,52].

Since the FTIR-ATR analysis allows to evaluate the structure of the sample surface with a depth of few  $\mu$ m, the following results are not quantitative, but only a qualitative evaluation of an increase in the structural order in the form of mesophase or crystalline  $\alpha$ -form is reported.

We first investigate the effect of different pressures on melt quenched PLLA. Figure 4.1 shows the FTIR-ATR spectra of melt-quenched sample treated for  $t_s$  3minutes with CO<sub>2</sub> at different pressures ( $t_n$ 0\_P\_3).



Figure 4. 1. FTIR-ATR spectra of sample  $t_n$  0 conditioned with CO<sub>2</sub> at different pressures for  $t_s$  3min

The untreated sample ( $t_s = 0$ ) shows no mesomorphic/crystalline band at 918-922 cm<sup>-1</sup> confirming the amorphous nature of the sample. By treatment with CO<sub>2</sub>, the band at 870 cm<sup>-1</sup>, shifts to higher wavenumbers, indicating an increase in the structural order. Treatment with CO<sub>2</sub> up to 5 MPa evidences formation of the mesomorphic band at 918 cm<sup>-1</sup>, which shifts to higher wavenumbers in case of sample treated with 6MPa, suggesting presence of also  $\alpha$ -crystals in this sample. That means the formation of mesomorphic phase instead of  $\alpha$ -crystals is favored at  $T_{amb}$  by a 3 min treatment with CO<sub>2</sub> up to 5 MPa, while an increase in the pressure promotes crystallization in  $\alpha$ -form.

The influence of homogeneous crystal nuclei on mesophase formation is presented in Figure 4.2. Samples with different amounts of homogeneous crystal nuclei, developed at 60 °C for  $t_n = 0$ , 0.5 and 2 hours, were treated with 5 MPa of CO<sub>2</sub> for  $t_s = 3$  min. Dotted curves referring to the polymer not conditioned with CO<sub>2</sub> ( $t_s = 0$ ) are also reported for comparison.



Figure 4. 2. FTIR-ATR spectra of samples with  $t_n = 0$ , 0.5 and 2h conditioned with 5MPa of CO<sub>2</sub> for  $t_s = 3min$  (solid curves). Samples  $t_n = 0$  and 0.5 untreated with CO<sub>2</sub> (dotted curves).

Results presented in Figure 4.2 show that mesophase is not present before treatment with  $CO_2$ , since the band at 918 cm<sup>-1</sup> is not visible in melt quenched and  $t_n = 0.5$  untreated samples (dotted black and red curves respectively). This results was *a priori* unexpected, since appearance of a FTIR band at 918 cm<sup>-1</sup> was reported for amorphous PLLA subjected to prolonged aging at 51 °C [43]. After  $t_s = 3$  min in presence of 5 MPa of  $CO_2$ , a shift in the band at 870 cm<sup>-1</sup> occurs and all the three samples display the mesomorphic band at 918 cm<sup>-1</sup>, indicating and increase in the structural order in form of mesophase. The three treated spectra do not display any sizeable difference or shift in wavenumbers, leading to the conclusion that HCN already present in the samples do not affect the kinetics of formation of the mesophase under the chosen experimental conditions.

#### Influence of CO<sub>2</sub>-induced mesophase on non-isothermal crystallization of PLLA

Since mesophase is known to increase the crystallization rate of PLLA, samples were studied via differential scanning calorimetry to clarify the effect of CO<sub>2</sub> conditioning on non-isothermal crystallization of PLLA. As before, all samples were degassed at room temperature for one week before analyses, to allow release of CO<sub>2</sub> and attain  $\alpha''$ -mesophase. First, the influence of CO<sub>2</sub> pressure and  $t_s$  on melt quenched PLLA is studied, then the analysis focuses on the interplay between HCN and mesophase on thermal properties of PLLA. Figure 4.3 shows heat flow curves of melt quenched PLLA ( $t_n = 0$ ) treated with CO<sub>2</sub> from 3 to 6 MPa for different  $t_s$ .



Figure 4. 3. Heat flow curves upon heating at  $20K \cdot min^{-1} a$ ) melt quenched sample  $t_n 0_t_s 0 b$ ) sample  $t_n 0$  conditioned with CO<sub>2</sub> at different pressures for various  $t_s$ 

Upon heating at 20 K·min<sup>-1</sup>, melt quenched sample (Fig 4.3 a) displays the typical  $T_g$  of amorphous PLLA around 60°C, without other significant thermal event in the temperature range of analysis (0 – 200 °C). Conversely, CO<sub>2</sub>-treated samples display multiple main transition: i)  $T_g$ ; ii) cold crystallization at temperature ( $T_c$ ) peaked around 100-120°C; and iii) crystal melting with main peak centered at 160°C ( $T_m$ ). In all the samples,  $T_g$  is followed by one or two endothermic peaks: the one at lower temperature (55-60 °C) is associated to enthalpy recovery [53–55], the one at higher temperature (around 63 °C) is possibly linked to the mesophase [39,45].

The double endothermic peak at  $T_g$ , can be associated also to the presence of both interspherulitic and intraspherulitic amorphous phases [56]. The low temperature transition is related to a bulk like non-confined process, while the higher endothermic peak is assigned to an amorphous phase confined between spherulite lamellae. This is confirmed by the presence of a peak at higher temperature in the heath flow curves of samples treated at pressures above 3MPa, where the amorphous phase is confined between crystals grown during conditioning, as demonstrated by results showed in Figure 4.6.

However, the experimental data gained to date do not allow quantitative analysis of the thermal events in this temperature range, for which thorough investigation is planned, via temperature-dependent infrared spectroscopy and X-ray diffraction analysis, coupled with conventional and temperature-modulated calorimetry.

Results shown in Figure 4.3 b, reveal an influence of  $t_s$  on crystallization rates. At parity of CO<sub>2</sub> pressure,  $T_c$  progressively decreases by increasing  $t_s$ . The CO<sub>2</sub> conditioning enhances mesophase formation, which in turn promotes crystallization by the formation of local ordering.

Not only  $t_s$  is a key feature to control the amount of mesomorphic chain reorganization, but also gas pressure influences the crystallization rates. As shown in Figure 4.4, for sample  $t_n = 0$  treated

with  $CO_2$  for  $t_s = 3 \text{ min}$ ,  $T_c$  substantially shifts to lower temperatures by increasing the pressure from 3 to 5 MPa and the exothermic peak becomes sharper.



Figure 4. 4. Heat flow curves of sample t<sub>n</sub> 0 conditioned for t<sub>s</sub> 3min by varying CO<sub>2</sub> pressure

The increase in  $CO_2$  pressure determines an increase in the gas sorption rates and in the gas concentration within the polymer. Then, an increase in the gas pressure improves the chain mobility and reorganization in the form of mesophase which in turn enhances crystallization rates.

Sample treated with 6 MPa of CO<sub>2</sub> for  $t_s = 3 \min (t_n 0_6 t_s 3)$ , displays a different behavior. No cold crystallization peak is detected, indicating that the sample does not crystallize upon heating. This result, coupled with the shift in the mesomorphic/crystalline band from 918 to 921 cm<sup>-1</sup> in the FTIR-ATR spectrum, suggests crystallization of the polymer into  $\alpha$ -modification during CO<sub>2</sub> treatment. The same thermal behavior is displayed after a 5 minutes treatment under 5 MPa pressure, as showed in Fig 4.3.

This effect of  $CO_2$  conditioning on  $T_c$ , measured as the temperature of the peak, for the melt quenched sample is rationalized in Figure 4.5.



**Figure 4. 5.**  $T_c$  of initially amorphous PLLA ( $t_n = 0$ ) after CO<sub>2</sub> conditioning at the indicated pressures, as a function of  $t_s$ . Data were derived from DSC curves shown in Figure 4.3 b.

It is clearly seen that 6MPa pressure is more effective in decreasing  $T_c$  at low  $t_s$  than the other pressures, since after 1 minute treatment it lowers  $T_c$  by 30 K if compared to sample treated with CO<sub>2</sub> at 3 MPa. This sizable enhancement in the crystallization rate displayed at high pressures such as 6 MPa carries also, as a drawback, that the maximum exposure time to CO<sub>2</sub> is reduced, hence fine tuning of the crystallization properties is limited. For  $t_s$  higher than 1 minute under 6 MPa of CO<sub>2</sub>, or 3 minutes for a pressure of 5 MPa, samples crystallize in the stable  $\alpha$ -modification form within the pressure vessel, which reduces the possibility of adjusting crystallization kinetics under higher pressures. By increasing treatment time, the lowest  $T_c$  of 95°C is reached after a treatment under 4 MPa for a  $t_s$  of 20 minutes. Results shown in Figure 4.5 suggest that the crystallization kinetics can be easily tuned by varying CO<sub>2</sub> pressure and exposure time.

Some crystallization in  $\alpha$ -form can be detected in nearly all analyzed samples, and quantified by comparison of the enthalpy of melting ( $\Delta H_m$ ) and enthalpy of cold crystallization ( $\Delta H_c$ ), measured by integration of the corresponding endothermic/exothermic peaks of the DSC plots shown in Figure 4.3. Data are presented in Figure 4.6 as a function of  $t_s$ .



**Figure 4. 6.**  $\Delta H_m - \Delta H_c$  of initially amorphous PLLA ( $t_n = 0$ ) after CO<sub>2</sub> conditioning at the indicated pressures, as a function of  $t_s$ . Data were derived from DSC curves shown in Figure 4.3 b.

 $\Delta H_{\rm m}$  values higher than 0 reveal melting of  $\alpha$ -crystals developed in the pressure vessel, which adds to melting of crystals formed upon DSC heating. CO<sub>2</sub> treatment leads not only the growth of the clathrate structure which evolves into the *emptied form* of PLLA-CO<sub>2</sub> complex, but also to formation of  $\alpha$ -crystals. This coexistence of  $\alpha$ "-modification and  $\alpha$ -form is displayed in different amount by the samples treated at each pressure.

This behavior is particularly evident after the conditioning at high pressures, like 5 or 6 MPa with, as an example, a value of  $\Delta H_{\rm m} - \Delta H_{\rm c}$  equals to 22 J·g<sup>-1</sup> after 1 minute conditioning under 6 MPa of CO<sub>2</sub>. Samples conditioned with 4 MPa of CO<sub>2</sub> display an initial absence of  $\alpha$ -crystals developed during CO<sub>2</sub> treatment, with  $\Delta H_{\rm m} - \Delta H_{\rm c}$  values increasing with  $t_{\rm s}$ . Conversely, conditioning under pressure of 3 MPa leads to minor, if any, growth of  $\alpha$ -crystals within the pressure vessel, as demonstrated by  $\Delta H_{\rm m} - \Delta H_{\rm c}$  values near to zero after every  $t_{\rm s}$ . The role of  $\alpha$ "-mesophase in accelerating growth of  $\alpha$ -crystals in PLLA is probed by comparison of samples containing no  $\alpha$ -modifications (30-40 MPa,  $t_{\rm s}$  =1 min), which all evidence a sizable a cold crystallization exotherm, with the i.e. initially amorphous polymer, only quenched from the melt without exposure to CO<sub>2</sub>, (Figure 4-3-a) that reveal no sign of cold crystallization upon heating, and obviously of no crystal melting. However, the influence of small amounts of  $\alpha$ -crystals in promoting further crystal growth upon heating needs to be defined and separated, for a full understanding of the role of  $\alpha$ "-mesophase

in accelerating crystallization rate of PLLA. Therefore, further experiments are planned, using lower  $CO_2$  pressures and/or treatment times, to attain samples containing  $\alpha''$ -mesophase only, in combination with WAXS and FTIR analyses, needed to probe the absence of measurable amounts of  $\alpha''$ -crystals.

#### Interplay between α"-mesophase and HCN

Combined effect of mesophase and HCN on crystallization kinetics of PLLA was investigated by thermally annealing the polymer at 60 °C for  $t_n = 0$ , 0.5 and 2 hours to form HCN, followed by conditioning under CO<sub>2</sub> at various pressures at room temperature, and degassed for one week, for  $\alpha$ "-mesophase formation. Figure 4.7 shows the influence of coupling thermal pre-treatment and mesophase formation on crystallization rates, by treating samples with different  $t_n$  for a  $t_s$  of 3 minutes under pressures from 3 to 6 MPa. Since for the aim of this research,  $t_s = 3$  min represents the best balance between fastness in experiments and yield in mesophase formation, the results are discussed by fixing  $t_s$  to this value.



**Figure 4. 7.** a) Heat flow curves of samples with  $t_n 0$ , 0.5 and 2h conditioned for  $t_s$  3min by varying CO<sub>2</sub> pressure; b)  $T_c$  derived from DSC curves shown in Figure 4.6 a as a function of  $t_n$  and CO<sub>2</sub> pressure

The DSC plots are presented in Figure 4.7-a, whereas the exothermic peak temperatures are plotted as function of nucleation time at 60 °C ( $t_n$ ) in Figure 4.7-b. Comparison between  $\Delta H_m$  and  $\Delta H_c$  indicates partial crystallization of the polymer in  $\alpha$ -modification due to CO<sub>2</sub> conditioning in the pressure vessel.  $\Delta H_m - \Delta H_c$  amounts to 17, 1, and 0 J/g, when PLLA is treated for 3 min with CO<sub>2</sub> at 5, 4, and 3 MPa, respectively, independently of  $t_n$ . This indicates that prior formation of HCN does not affect crystallization of PLLA in  $\alpha$ -crystals in the presence of CO<sub>2</sub>. The influence of  $t_n$  on crystallization peak temperature upon DSC heating also appears minor, compared to the much faster

crystallization kinetics attained by variation of CO<sub>2</sub> pressure, but still some effect appears evident from the data shown in Figure 4.7. The presence of HCN in samples  $t_n = 0.5$  and  $t_n = 2$  determines a faster crystallization when compared to  $t_n = 0$  sample at the same pressure. Both in case of CO<sub>2</sub> conditioning under 4 and 5 MPa, nucleated samples display a decrease in  $T_c$  of about 5 K. In case of 3 MPa pressure, conversely, the broadness of the exothermic peak does not allow a precise estimation of  $T_c$ , which appears roughly constant at around 130°C. The exothermic peak at  $t_n = 0$  appears larger than in the samples containing HCN, a result that deserves further investigation for a thorough rationalization.

# **4.3 Conclusions**

PLLA samples with a thickness of 0.5 mm were conditioned at room temperature with CO<sub>2</sub> pressure from 3 to 6 MPa then degassed, to study the influence of  $\alpha''$ -mesophase on thermal properties and crystallization kinetics of PLLA. In addition, preliminary results about the influence of previously developed HCN on mesophase formation was shown. FTIR-ATR analysis revealed the appearance of a band related to CO<sub>2</sub>-induced mesophase in all the samples, except for the one conditioned for  $t_s \ge 3$  under 6 MPa, where the polymer completely crystallizes in the form of  $\alpha$ -crystals during conditioning. This indicates that the upper limit in the processing conditions for mesophase growth at ambient temperature is represented by 1 minute when a CO2 pressure of 6 MPa is applied.

The thermal properties of PLLA containing  $\alpha''$ -mesophase were studied by DSC to investigate the influence of both  $t_s$  and CO<sub>2</sub> pressure on the crystallization rate of PLLA. The cold crystallization peak temperature  $T_c$  decreases by increasing  $t_s$  and conditioning pressures, indicating that the mesomorphic chain reorganization to  $\alpha$ -crystals is favored by higher CO<sub>2</sub> concentrations within the sample. The study of interplay of HCN and mesophase on thermal properties revealed an influence of HCN in lowering  $T_c$  of about 5 K if compared to melt-quenched polymer, but very minor differences are displayed by increasing the nucleation time at 60 °C beyond 0.5 h, at least under the chosen experimental conditions.

The study presented in this chapter provides the basis of a novel, cost-effective and green process to tune thermal properties of PLLA. The short time and low pressures needed to reach highly enhanced crystallization rates, pave the way for a methodology to widen PLLA application by easy changing processing conditions in a few minutes and with a reduced amount of gas with the added value of a tuning of properties at a controllable level.

# **4.4 Supporting Information**

#### The optic foaming

Initial attempts to foam aged PLLA in the mini-batch pressure vessel revealed some limitation of the equipment on the temperature control. In particular, the samples experienced large temperature variation during the pressurization stages. We hence designed a new pressure vessel, which we called "optic foaming", that must satisfy three main functions: i) optimal temperature control, ii) reproducibility of the experiments and iii) optical access to the samples during processing. Furthermore, the designing approach was to minimize the volume available to the blowing agent, to reduce thermal disturbance during the steep pressure changes (at both pressure increase and decrease) and to minimize the optical disturbance of the high-density blowing agent, subjected to thermal fluctuations, unavoidable during the foaming operations.

To achieve an optimal temperature control, one important feature of this design is represented by the heating system. The pressure vessel is equipped with an oil bath heating system and an internal recirculating jacket. Together with the temperature control, test reproducibility also requires a precise pressure control during all the processing stages. To this aim, another important feature of the optic foaming pressure vessel design is the use of two two-ways solenoid valves activated by electric actuators for the gas inlet and the gas discharge. The use of this system is required to avoid any effect of the manual operator in case manual valves are utilized. Last, but not least, the optical access, which is also the novelty of this system, allows optical microscopy analysis, under pressure and temperature both in static and dynamic (scanning) mode. The optical access is achieved by installation of two optical sapphire windows and a sample holder designed to allow the image acquisition both under reflected or transmitted light.

#### **Design and apparatus**

The apparatus is showed in Figure S4.1. It consists of a hollow cylinder with an external diameter of 70mm and an inner diameter of 30 mm and a height of 45 mm resulting in a volume of  $4 \text{ cm}^3$ . The top access port is used for the introduction of the sample and is equipped with a quick connection to ensure fast introduction and removal of the sample.



Figure S4. 1. Optic foaming equipment

Two ports on the sides connected to two high pressure solenoid valves activated by electric actuators (Keihin Valve Corp. Mod. SSPDH3-4015-8GUJ-X), used for the gas inlet and discharge. Both valves can be further equipped with a needle valve for flow reduction.

A detailed picture of the bottom is showed in Figure S4.2 to show the access ports. The five ports are occupied by: 1) thermal oil tubes (oil inlet and outlet); 2) an optical sapphire window for the light source in transmittance experiments; 3) a pressure transducer (Gefran, Mod. TK-E-7-E-B35D-M-V); 4) the temperature sensor (Gefran, Mod. TR1M-A-2-B-A-C-E).



Figure S4. 2. Bottom view of the reactor with connection ports

An oil bath heating circulator (Julabo Magio MX BC6) with a silicone thermal oil is adopted for temperature control. As mentioned above, the aim of designing the novel apparatus was to ensure an optimal temperature control in terms of both temperature uniformity and minimization of the thermal fluctuation. While thermal fluctuation minimization is assured by the oil recirculation and bath heating circulator, temperature uniformity requires a suitable design of the pressure vessel. In particular, sources of thermal non-uniformity are the connections to the valves and the sensors. To study the thermal problem and the effect of cold spot on the thermal uniformity, a numerical simulation with a finite element software (COMSOL) was in order. Figure S4.3 shows the comparison between two different pressure vessel wall thickness and the corresponding solutions of the thermal problem in stationary conditions when two cold spots are present, due to the connections to the gas lines.



Figure S4. 3. Thermal stability studies by COMSOL simulations

The solutions depicted in Fig S4.3-a demonstrate how a wall thickness of 12mm is not sufficient to attain thermal uniformity, which is in fact attained when a thicker wall of 20 mm is utilized (see Fig.S4.3-b).

As the reactor is equipped with two customized sapphire optical windows, studies on the effect of high pressures of  $CO_2$  on the crystallization rate of PLLA and of spherulites growth rate can be performed. The optical system allows also following the ongoing foaming as well as the sample swelling due to  $CO_2$  sorption. To use the apparatus in transmitted light optical observation mode, a tailored design sample holder, showed in Figure S4.4, is required.



Figure S4. 4. Sample holder rendering

The sample holder consists of a cover glass for microscopy, mounted on a round sample holder, showed in Fig S4.4a. The round sample holder is then placed in a frame by an interlocking system as showed in Fig S4.4b and c. This configuration satisfies the two functions to reduce mobility of the sample and to allow light transmission.

# **4.5 References**

- [1] J.W. Leenslag, A.J. Pennings, R.R.M. Bos, F.R. Rozema, G. Boering, Resorbable materials of poly (L-lactide): VII. In vivo and in vitro degradation, Biomaterials. 8 (1987) 311–314.
- [2] J.W. Leenslag, A.J. Pennings, R.R.M. Bos, F.R. Rozema, G. Boering, Resorbable materials of poly (L-lactide). VI. Plates and screws for internal fracture fixation, Biomaterials. 8 (1987) 70–73.
- [3] R.A. Gross, B. Kalra, Biodegradable polymers for the environment, Science (80-.). 297 (2002) 803–807.
- [4] D. Garlotta, A literature review of poly (lactic acid), J. Polym. Environ. 9 (2001) 63–84.
- [5] R. Auras, B. Harte, S. Selke, An overview of polylactides as packaging materials, Macromol. Biosci. (2004). https://doi.org/10.1002/mabi.200400043.
- [6] J.-W. Rhim, H.-M. Park, C.-S. Ha, Bio-nanocomposites for food packaging applications, Prog. Polym. Sci. 38 (2013) 1629–1652.
- [7] T. Iwata, Y. Doi, Morphology and enzymatic degradation of poly (L-lactic acid) single crystals, Macromolecules. 31 (1998) 2461–2467.
- [8] G. Liu, X. Zhang, D. Wang, Tailoring crystallization: towards high-performance poly (lactic acid), Adv. Mater. 26 (2014) 6905–6911.
- [9] H. Bai, C. Huang, H. Xiu, Q. Zhang, H. Deng, K. Wang, F. Chen, Q. Fu, Significantly improving oxygen barrier properties of polylactide via constructing parallel-aligned shishkebab-like crystals with well-interlocked boundaries, Biomacromolecules. 15 (2014) 1507– 1514.
- [10] H. Cai, V. Dave, R.A. Gross, S.P. McCarthy, Effects of physical aging, crystallinity, and orientation on the enzymatic degradation of poly (lactic acid), J. Polym. Sci. Part B Polym. Phys. 34 (1996) 2701–2708.
- [11] A.M. Harris, E.C. Lee, Improving mechanical performance of injection molded PLA by controlling crystallinity, J. Appl. Polym. Sci. 107 (2008) 2246–2255.
- [12] M.L. Di Lorenzo, M. Cocca, M. Malinconico, Crystal polymorphism of poly(L-lactic acid) and its influence on thermal properties, Thermochim. Acta. (2011). https://doi.org/10.1016/j.tca.2010.12.027.
- [13] M. Cocca, M.L. Di Lorenzo, M. Malinconico, V. Frezza, Influence of crystal polymorphism on mechanical and barrier properties of poly(L-lactic acid), Eur. Polym. J. (2011). https://doi.org/10.1016/j.eurpolymj.2011.02.009.
- [14] M. Cocca, R. Androsch, M.C. Righetti, M. Malinconico, M.L. Di Lorenzo, Conformationally disordered crystals and their influence on material properties: The cases of isotactic

polypropylene, isotactic poly(1-butene), and poly(L-lactic acid), J. Mol. Struct. (2014). https://doi.org/10.1016/j.molstruc.2014.02.038.

- [15] G. Perego, G.D. Cella, C. Bastioli, Effect of molecular weight and crystallinity on poly (lactic acid) mechanical properties, J. Appl. Polym. Sci. 59 (1996) 37–43.
- [16] M.L. Di Lorenzo, R. Androsch, Industrial Applications of Poly (lactic acid), 2018.
- [17] D. da Silva, M. Kaduri, M. Poley, O. Adir, N. Krinsky, J. Shainsky-Roitman, A. Schroeder, Biocompatibility, biodegradation and excretion of polylactic acid (PLA) in medical implants and theranostic systems, Chem. Eng. J. 340 (2018) 9–14. https://doi.org/https://doi.org/10.1016/j.cej.2018.01.010.
- H. Li, M.A. Huneault, Effect of nucleation and plasticization on the crystallization of poly(lactic acid), Polymer (Guildf). 48 (2007) 6855–6866. https://doi.org/10.1016/j.polymer.2007.09.020.
- [19] M.L. Di Lorenzo, A. Longo, N, N-Diethyl-3-methylbenzamide (DEET): A mosquito repellent as functional plasticizer for poly (L-lactic acid), Thermochim. Acta. 677 (2019) 180– 185.
- [20] I. Bonadies, A. Longo, R. Androsch, M.L. Di Lorenzo, Biodegradable electrospun PLLA fibers containing the mosquito-repellent DEET, Eur. Polym. J. 113 (2019) 377–384. https://doi.org/10.1016/j.eurpolymj.2019.02.001.
- [21] M. Penco, G. Spagnoli, I. Peroni, M.A. Rahman, M. Frediani, W. Oberhauser, A. Lazzeri, Effect of nucleating agents on the molar mass distribution and its correlation with the isothermal crystallization behavior of poly (L-lactic acid), J. Appl. Polym. Sci. 122 (2011) 3528–3536.
- [22] A. Pei, Q. Zhou, L.A. Berglund, Functionalized cellulose nanocrystals as biobased nucleation agents in poly (L-lactide)(PLLA)–Crystallization and mechanical property effects, Compos. Sci. Technol. 70 (2010) 815–821.
- [23] M. Nofar, A. Tabatabaei, A. Ameli, C.B. Park, Comparison of melting and crystallization behaviors of polylactide under high-pressure CO<sub>2</sub>, N<sub>2</sub>, and He, AIP Conf. Proc. 1593 (2014) 320–323. https://doi.org/10.1063/1.4873791.
- [24] M. Nofar, W. Zhu, C.B. Park, Effect of dissolved CO<sub>2</sub> on the crystallization behavior of linear and branched PLA, Polymer (Guildf). 53 (2012) 3341–3353. https://doi.org/10.1016/j.polymer.2012.04.054.
- [25] L. Yu, H. Liu, K. Dean, Thermal behaviour of poly(lactic acid) in contact with compressed carbon dioxide, Polym. Int. 58 (2009) 368–372. https://doi.org/10.1002/pi.2540.
- [26] Y.-M. Corre, A. Maazouz, J. Reignier, J. Duchet, Influence of the chain extension on the crystallization behavior of polylactide, Polym. Eng. \& Sci. 54 (2014) 616–625. https://doi.org/https://doi.org/10.1002/pen.23595.

- [27] C. Zhao, D. Wu, N.A.N. Huang, H. Zhao, Crystallization and thermal properties of PLLA comb polymer, J. Polym. Sci. Part B Polym. Phys. 46 (2008) 589–598.
- [28] N. Burgos, D. Tolaguera, S. Fiori, A. Jiménez, Synthesis and characterization of lactic acid oligomers: Evaluation of performance as poly (lactic acid) plasticizers, J. Polym. Environ. 22 (2014) 227–235.
- [29] M.L. Di Lorenzo, R. Androsch, Accelerated crystallization of high molar mass poly (L/Dlactic acid) by blending with low molar mass poly (L-lactic acid), Eur. Polym. J. 100 (2018) 172–177.
- [30] E. Schulz, B. Wunderlich, Macromolecular physics, Vol. 2 crystal nucleation, growth, annealing, Wiley Online Library, 1977.
- [31] C. Schick, R. Androsch, J.W.P. Schmelzer, Homogeneous crystal nucleation in polymers, J. Phys. Condens. Matter. 29 (2017) 453002.
- [32] R. Androsch, M.L. Di Lorenzo, Crystal nucleation in glassy poly(L-lactic acid), Macromolecules. (2013). https://doi.org/10.1021/ma401036j.
- [33] A. Longo, G. Dal Poggetto, M. Malinconico, P. Laurienzo, E. Di Maio, M.L. Di Lorenzo, Enhancement of crystallization kinetics of poly(L-lactic acid) by grafting with optically pure branches, Polymer (Guildf). 227 (2021) 123852.
   https://doi.org/https://doi.org/10.1016/j.polymer.2021.123852.
- [34] M.L. Di Lorenzo, R. Androsch, Influence of α'-/α-crystal polymorphism on properties of poly(L-lactic acid), Polym. Int. (2019). https://doi.org/10.1002/pi.5707.
- [35] M.L. Di Lorenzo, R. Androsch, Crystallization of Poly(lactic acid), in: Biodegrad. Polyesters, John Wiley & Sons, Ltd, 2015: pp. 109–130. https://doi.org/https://doi.org/10.1002/9783527656950.ch5.
- [36] H. Marubayashi, S. Asai, M. Sumita, Crystal structures of poly (L-lactide)–CO<sub>2</sub> complex and its emptied form, Polymer (Guildf). 53 (2012) 4262–4271.
- [37] H. Marubayashi, S. Asai, M. Sumita, Guest-induced crystal-to-crystal transitions of Poly (Llactide) complexes, J. Phys. Chem. B. 117 (2013) 385–397.
- [38] Y. Zheng, C.-L. Zhang, Y.-Z. Bao, G.-R. Shan, P.-J. Pan, Temperature-dependent Crystallization and Phase Transition of Poly (L-lactic acid)/CO<sub>2</sub> Complex Crystals, Chinese J. Polym. Sci. 39 (2021) 484–492.
- [39] G. Stoclet, R. Seguela, J.-M. Lefebvre, C. Rochas, New Insights on the Strain-Induced Mesophase of Poly(D,L-lactide): In Situ WAXS and DSC Study of the Thermo-Mechanical Stability, Macromolecules. 43 (2010) 7228–7237. https://doi.org/10.1021/ma101430c.
- [40] G. Stoclet, R. Seguela, J.-M. Lefebvre, S. Elkoun, C. Vanmansart, Strain-induced molecular ordering in polylactide upon uniaxial stretching, Macromolecules. 43 (2010) 1488–1498.
- [41] J. Hu, T. Zhang, M. Gu, X. Chen, J. Zhang, Spectroscopic analysis on cold drawing-induced

PLLA mesophase, Polymer (Guildf). 53 (2012) 4922-4926.

- [42] J. Zhang, Y. Duan, A.J. Domb, Y. Ozaki, PLLA Mesophase and Its Phase Transition Behavior in the PLLA-PEG-PLLA Copolymer As Revealed by Infrared Spectroscopy, Macromolecules. 43 (2010) 4240–4246. https://doi.org/10.1021/ma100301h.
- [43] T. Zhang, J. Hu, Y. Duan, F. Pi, J. Zhang, Physical Aging Enhanced Mesomorphic Structure in Melt-Quenched Poly(L-lactic acid), J. Phys. Chem. B. 115 (2011) 13835–13841. https://doi.org/10.1021/jp2087863.
- [44] Q. Lan, Y. Li, Mesophase-Mediated Crystallization of Poly(L-lactide): Deterministic Pathways to Nanostructured Morphology and Superstructure Control, Macromolecules. 49 (2016) 7387–7399. https://doi.org/10.1021/acs.macromol.6b01442.
- [45] Q. Lan, Y. Li, H. Chi, Highly Enhanced Mesophase Formation in Glassy Poly(L-lactide) at Low Temperatures by Low-Pressure CO<sub>2</sub> That Provides Moderately Increased Molecular Mobility, Macromolecules. 49 (2016) 2262–2271. https://doi.org/10.1021/acs.macromol.6b00044.
- [46] H. Marubayashi, S. Akaishi, S. Akasaka, S. Asai, M. Sumita, Crystalline structure and morphology of poly(L-lactide) Formed under high-pressure CO<sub>2</sub>, Macromolecules. 41 (2008) 9192–9203. https://doi.org/10.1021/ma800766h.
- [47] S. Li, T. Chen, X. Liao, W. Han, Z. Yan, J. Li, G. Li, Effect of Macromolecular Chain Movement and the Interchain Interaction on Crystalline Nucleation and Spherulite Growth of Polylactic Acid under High-Pressure CO<sub>2</sub>, Macromolecules. 53 (2020) 312–322. https://doi.org/10.1021/acs.macromol.9b01601.
- [48] Luminy® PLA neat resins, (n.d.). https://totalcorbion.4netacc.com/media/iufhvey2/factsheet\_luminy-pla-neat-resins\_20190903.pdf.
- [49] D. Tammaro, V. Contaldi, M.G.P. Carbone, E. Di Maio, S. Iannace, A novel lab-scale batch foaming equipment: The mini-batch, J. Cell. Plast. 52 (2016) 533–543. https://doi.org/10.1177/0021955X15584654.
- [50] J. Zhang, Y. Duan, H. Sato, H. Tsuji, I. Noda, S. Yan, Y. Ozaki, Crystal modifications and thermal behavior of poly (L-lactic acid) revealed by infrared spectroscopy, Macromolecules. 38 (2005) 8012–8021.
- [51] B. Xue, L. Xie, J. Zhang, Detailed molecular movements during poly (L-lactic acid) coldcrystallization investigated by FTIR spectroscopy combined with two-dimensional correlation analysis, RSC Adv. 7 (2017) 47017–47028.
- [52] V. Krikorian, D.J. Pochan, Crystallization behavior of poly (L-lactic acid) nanocomposites: nucleation and growth probed by infrared spectroscopy, Macromolecules. 38 (2005) 6520– 6527.
- [53] P. Pan, B. Zhu, Y. Inoue, Enthalpy relaxation and embrittlement of poly (L-lactide) during

physical aging, Macromolecules. 40 (2007) 9664-9671.

- [54] H.M.N. Iqbal, C. Sungkapreecha, R. Androsch, Enthalpy relaxation of the glass of poly (Llactic acid) of different D-isomer content and its effect on mechanical properties, Polym. Bull. 74 (2017) 2565–2573.
- [55] X. Monnier, D. Cavallo, M.C. Righetti, M.L. Di Lorenzo, S. Marina, J. Martin, D. Cangialosi, Physical aging and glass transition of the rigid amorphous fraction in poly (L-lactic acid), Macromolecules. 53 (2020) 8741–8750.
- [56] Y. Wang, J.L. Gómez Ribelles, M. Salmerón Sánchez, J.F. Mano, Morphological contributions to glass transition in poly (L-lactic acid), Macromolecules. 38 (2005) 4712– 4718.

# **Chapter 5**

# Conclusions

The research here presented provides methodologies to modulate PLLA thermal properties and its foam morphology by inducing chain reorganization and improving crystallization rates. The novelty of the approaches is represented from the production of a material with tunable properties with no need to compound with external additives that can alter its biocompatibility and recycling process. Simple modification of the polymer chain by adding side PLLA branches or by conditioning the polymer with low pressure of  $CO_2$  allows to modulate the crystallization rates; moreover, specific thermal treatments can tailor chain reorganization and allow fine tuning of foam morphology.

To enhance the crystallization rate of PLLA by introducing pure short chain branches, a biobased PLLA copolymer was prepared by a radical functionalization with itaconic anhydride (IAH) and then by nucleophilic attack with a tailor-made optically pure PLLA with a molar mass  $M_n = 4$ kDa. The efficiency of grafting was confirmed FTIR-ATR coupled to NMR analysis and to gel permeation chromatography. The amount of grafted IAH was quantified as 0.5% via UV-Vis, which corresponds to one IAH grafted every 24 repeating units of PLLA. The synthesized graft copolymer displays a higher spherulites growth rate with respect not only to the commercial grade, but also to a binary blend with the same nominal composition. The role played by the short branches in favoring crystal growth was rationalized as enhanced molecular nucleation: the short and regular side chains act as molecular nuclei that favor crystallization of the main chain backbone, proving the efficiency of grafting PLLA with optically pure short branches in improving the poor crystallization kinetics of PLLA.

The influence of chain reorganization on foam morphology was studied by inducing a local alignment of polymer chains in the form of nano-sized aggregates, called homogeneous crystal nuclei (HCN), with a thermal treatment at the glass transition temperature,  $T_g = 60$  °C, for nucleation times of 0.5, 2 and 4 hours. As expected, HCN density increases with nucleation time, and HCN can promote the growth of crystals that can be controlled by thermal-pressure history of the experiment. Nucleated samples were then physical foamed with scCO<sub>2</sub> at a pressure of 10 MPa and a temperature of 120 °C and analysis of sample morphology revealed that HCN act as heterogeneous nucleation sites not only for crystals, but also for bubbles. Increasing the nucleation time, foamed samples display a decrease in cell size and larger bubble density. In particular, samples nucleated for 2 and 4

hours show a bi-modal morphology, with the bulk characterized from bigger cells with an average diameter of 50–70  $\mu$ m and crystal aggregates, i.e. spherulites grow during the sorption step, surrounded by smaller stamen-like cells of few  $\mu$ m in diameter. These results demonstrate that tailored foam morphology can be attained without addition of external nucleating agents. Worth also to say that this methodology can be exploited also for other semi crystalline polymers opening up the possibility in fine tuning the foam morphology, preserving at the same time the biocompatibility and biodegradability of bio-based polymers.

CO<sub>2</sub> not only represents a green and low cost foaming agent for PLLA, but it can also be exploited to induce tailored chain reorganization in the polymer chain. By conditioning PLLA with pressures from 3 to 6 MPa of CO<sub>2</sub> at room temperature, the enhanced chain mobility induced by solubilization of the gas results in the formation of a clathrate crystal modification that, after degassing of CO<sub>2</sub>, transforms to  $\alpha''$ -crystal form. The latter is a metastable mesophase whose presence can be probed via FTIR and DSC measurements. By increasing the saturation time from 1 to 20 minutes, the amount of the formed mesophase increases and the same effect is obtained by increasing the pressure. The enhanced mesophase formation reflects on crystallization rates, since  $\alpha''$ -mesophase is metastable and upon heating transforms to  $\alpha$ -crystal. The study on the non-isothermal cold crystallization rate is affected by both CO<sub>2</sub> pressure and the saturation time. In particular, the cold crystallization temperature progressively lowers with increasing either the saturation time or the pressure, with the two lowest  $T_c$  detected as 100°C for the sample conditioned for 1 minute with a pressure of 6 MPa or 95°C for the saturated for 20 minutes with a pressure of 4 MPa.

If HCN are present in the sample before  $CO_2$  treatment, they play a cooperative role with the mesophase in increasing the crystallization rate. Thermal analysis of samples nucleated at 60 °C for 0.5 and 2 hours and then conditioned for 3 minutes with a  $CO_2$  pressure from 3 to 5 MPa, shows that the presence of HCN lowers the  $T_c$  by about 5 K if compared to the melt quenched sample.

Further analyses are planned to deeply clarify the influence of CO<sub>2</sub> induced mesophase on the crystallization mechanisms and crystal morphology. Temperature dependent infrared spectroscopy and X-ray diffraction analysis will elucidate the transformation of the mesophase in  $\alpha$ crystal, while the temperature modulated calorimetry is expected to clarify the role of mesophase in the double endothermic peak detected at  $T_g$ .

This study suggests the possibility of fine-tuning the crystallization rate of PLLA by adjusting pressure and treatment time allowing, at the same time, a tailored time/pressure balance, depending on the processing needs, with the added value of operating at room temperature and low CO<sub>2</sub> pressures. This appears as an easy, affordable, energy saver and low cost process to modulate the thermal properties and crystallization kinetics of PLLA.