ABSTRACT

STUDY OF POLY (L-LACTIC ACID)/POLY (D-LACTIC ACID) STEREOCOMPLEX AS NUCLEATING AGENT FOR POLY (L- LACTIC ACID) CRYSTALLIZATION

by

Yuan Lao

Poly (lactic acid) (PLA) is a biodegradable polymer with good renewability and processability. However, it has some drawbacks. The Poly (lactic acid) (PLA) stereocomplex formed via the interaction between optical isomers Poly (L-lactic acid) (PLLA) and Poly (D-lactic acid) (PDLA), provides improvements on PLA thermomechanical properties. To investigate the nucleating effect brought by the PLA stereocomplex, samples of PLLA blended with different content of PDLA are prepared by the solution casting method. With different cooling rates (5, 15, 25 °C/min), DSC non-isothermal crystallization experiments are performed. The results suggest that in the presence of the stereocomplex, the PLLA crystallization temperatures are found to be higher than that of pure PLLA. By annealing PLLA at different temperatures with the existence of the stereocomplex, the crystallization process is significantly expedited. Using hot stage polarized microscope, the increasing number of spherulites observed at higher temperature, confirms the enhancement on PLLA nucleation brought by the stereocomplex. Yet, the irregular morphology of crystallites may indicate that the

stereocomplex does not promote higher degree of crystallinity. Finally, the saturated nucleating effect is due to the unfavorably high molecular weights of PLLA and PDLA.

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CHAPTER 1

INTRODUCTION

1.1 Poly (lactic acid)

1.1.1 General

Novel science and technology pushes the socioeconomic development and operation efficiency of civilization. On the other hand, social and economic evolution drives scientists to find new edges. At present, being sustainable has become a main topic of new materials development, which is leading the exploration of renewable, reusable and bio-degradable polymers.

Poly (lactic acid), an aliphatic polyester, derived from natural products, such as corn starch, is a biodegradable polymer. Since the 1970's, PLA materials have been approved by US Food and Drug Administration (FDA) for direct use in containers for substances intended for human consumption. The final products of PLA degradation are water and carbon dioxide, which are non-toxic to human beings, as well as to ecosphere. Hence it can be produced as any one-off products that come in direct contact with humans, including food containers, cups, spoons, knives… Moreover, contributing to its processability, PLA can be formed into any desired shape, including film, board, pellets and fibers, by extrusion, injection molding, thermoforming, hot drawing, and solvent casting. [1] Due to the ease of synthesizing and processing, PLA is less energy-consuming than other polymers, consequently reducing air and water pollution. This feature surely can relieve the global warming effect and the over-consumption of fossil energy. [2] Fig. 1.1 shows the fossil energy needed for different polymers.

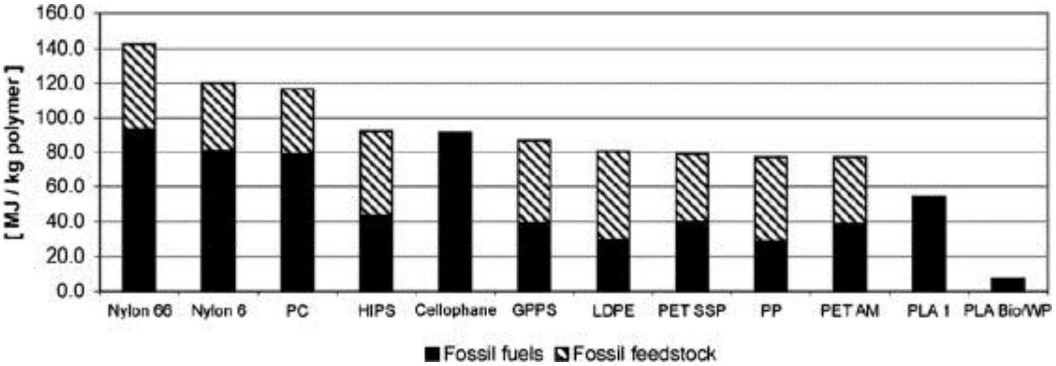


Fig. 1.1 Fossil energy needed for producing different materials. [2]

The monomer of PLA is lactic acid (2-hydroxy propionic acid), which can be taken from milk or similar dairy product. There are two different isomers exist with different optical configurations, L-lactic acid and D-lactic acid, which are shown in Fig. 1.2. [3]

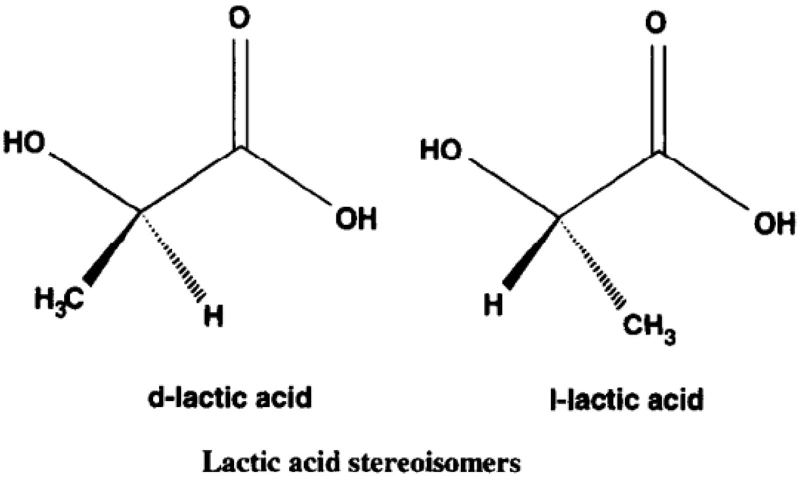


Fig. 1.2 Configurations of two lactic acid isomers. [3]

With L-lactic acid and D-lactic acid isomers, four different polymers can be produced: Semi-crystalline poly (L-lactic acid) (PLLA), regular chain structure polymer synthesized solely with L-lactic; Crystalline poly (D-lactic acid) (PDLA), regular chain structure polymer synthesized solely with D-lactic; and amorphous polymer poly (D, L-lactic acid) (PDLLA). Moreover, with meso-lactide as monomer, polymerized meso-PLA can be prepared. [1] Fig. 1.3 shows the chemical structure of PLA.

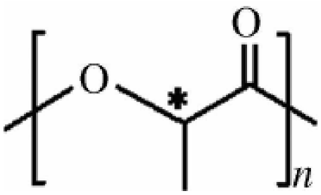


Fig. 1.3 Structure of PLA. [4]

1.1.2 Synthesis of PLA

Among various polymerization methods, direct polymerization and ring-opening polymerization are prevalent for synthesis of PLA.

The polymerization of PLA takes place between the –OH and –COOH groups in lactic acid. Fig. 1.4 shows the route of polymerization of PLA. [5]

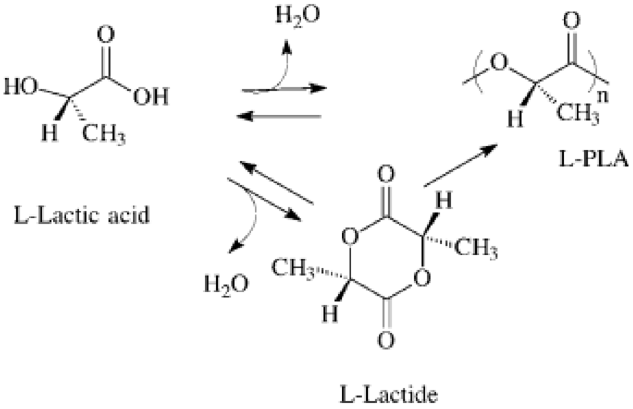


Fig. 1.4 PLA polymerization route sketch. [5]

Depending on the use of solvent, direct polymerization can be categorized into solution polycondensation and melt polycondensation.

In solution polycondensation, reaction takes place in the organic solvent which simply dissolves PLA but without other interactions. Water generated from the condensation will be removed to promote the progress of polymerization, and to obtain PLA with higher molecular weight. By selecting the appropriate catalyst and optimal conditions, the molecular weight of PLA can be as high as 300,000 g/mol, according to an early study by Ajioka et al, cited by Lin et al in their text book. [1]

Melt polycondensation of lactic acid can take place without the presence of organic solvent, but the reaction temperature must be above the melting temperature of polymer to keep it molten, and thus, allow for mobility and diffusion. The molecular weight of PLA can be > 500,000 g/mol under optimized conditions. [6]

Generally, direct polymerization process is easier, faster to perform, but the obstacles on removing water during reaction, and difficulties to control many parameters such as pressure, temperature, catalysts, has been limiting the polymerization on yielding higher molecular weight PLA. Ring-opening polymerization of lactide, thus, has been popularized among industries.

In the ring-opening polymerization, PLA is obtained from lactide, which, originates from oligomerization then dimerization of the lactic acid. With controlling the catalyst type, reaction time and temperatures, it becomes possible to obtain desired ratio and tacticity of D- and L-lactic acid unit in the final polymer product. [3]

Tin compounds have been widely used for catalyzing the PLA ring-opening polymerization, because of their low toxicity, high catalytic activity and the ability to yield high molecular weight polymers. [7]

In addition to the aforementioned polymerization methods, there are new approaches for synthesizing PLA polymers. The general routes of synthesizing PLLA and PDLA are shown in Fig. 1.5 [8] while a comparison between several PLA synthesis methods is given in Table 1.1. [1]

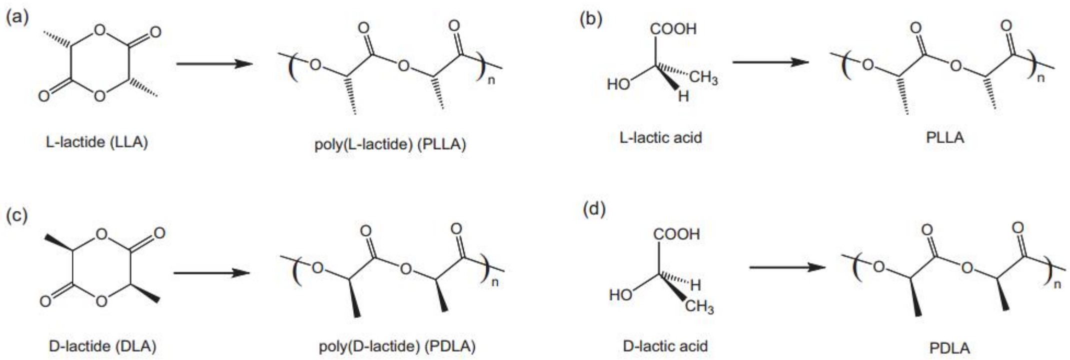


Fig. 1.5 General synthesis routes and structures of (a), (b), PLLA, and (c), (d), PDLA. [8]

Table 1.1 Comparison between different PLA synthesis methods [1]

Synthesis methods	Advantages	Disadvantages
Solution polycondensation.	Easy to control, economical.	Impurities, side reactions, pollution, low molecular weight product.
Melt polycondensation.		High reaction temperature, sensitive to reaction conditions, low molecular weight product.
Ring-opening polymerization.	High molecular weight product.	100% pure lactide monomer.
Biosynthesis.	One-step, efficient, non-toxic, no pollution, low cost, etc.	Under development.

1.1.3 Properties

In addition to the great degradability and processability, PLA also possesses other valuable physical, chemical and mechanical properties. PLA homopolymer has glass transition temperature (T_g) around 55 °C, and melting temperature (T_m) around 175 °C.

However, thermal properties such as T_g and Tm, and mechanical properties such as tensile and breaking strength, are affected by the polymer structure. The differences in molecular weight, crystalline structure (i.e. crystalline, semi crystalline, amorphous) and tacticity lead to differences in properties. [8] Table 1.2 lists several selected physical and chemical properties of PLA.

Table 1.2 Summary of selected physical and mechanical properties of PLLA, PDLA and PDLLA [8]

Properties	PLLA	PDLA	PDLLA
Crystalline structure	Semi crystalline	Crystalline	Amorphous
Solubility	Common organic solvents	Common organic solvents	Common organic solvents
Melting temperature / °C	Around 180	Around 180	Variable
Glass transition temperature / °C	55 - 60	50 - 50	Variable
Elongation at break / %	20 - 30	20-30	Variable
Breaking strength/ (g/d)	5.0 - 6.0	4.0 - 5.0	Variable

Even though PLA can be considered as a good renewable substitute for petroleum-based materials, some properties are still inferior to those of traditional polymer materials. PLA is brittle, showing low elongation strain at breaking point. Unless modified, it cannot be used as a proper substitute for applications requiring good elongation. [9] In addition, the heat distortion temperature is around 55 – 65 °C for most pure PLA homopolymers, narrowing and limiting their utilization range. [4]

To improve their general performance, considerable amount of research has been conducted. Perego et al. studied the effect of molecular weight and crystallinity on PLA mechanical properties. In their study, PLLA samples were prepared by injection molding method. The impact resistance was found to improve with molecular weight. [10]

Jonoobi et al. studied the mechanical properties of cellulose nanofiber-reinforced PLA. By blending the PLA matrix with cellulose nanofibers via twin screw extrusion method, which produced PLA with well-dispersed nanofibers with no agglomeration, they observed improvement on tensile strength. The tensile strength increased with nanofiber content. Moreover, they predicted that the improvement may be more remarkable with the more extended of fiber alignment. [11]

Shi et al. studied the increase in heat deflection temperature of reinforced PLA. PLA composites with 20 wt% of bamboo fiber and 20 wt% of talc were produced by compression molding. Heat deflection temperature of the composites showed an increase with over 40 °C, compared to pure PLA (63 °C). [12] It is noteworthy that talc can also act as a heterogeneous nucleating agent for PLA.

Similarly, Huda et al improved the thermal and mechanical properties and heat deflection temperature of PLA by incorporating kenaf fibers. Moreover, with the incorporation of fiber treated with both silane and alkali, the thermal and mechanical properties of PLA composite were further improved. [13]

Due to the rigidity and brittleness of PLA at room temperature, Hassouna et al. studied the plasticizing effect on PLA of grafting by hydroxyl-functionalized using reactive extrusion. Furthermore, the reactive mixing of PLA, maleic anhydride-grafted PLA copolymer (plasticizer), and PEG was performed. Results indicated an overall improvement on PLA's yield stress, when plasticized with 10wt% PEG and 10wt% maleic anhydride-grafted PLA copolymer. However, the plasticizer steeply reduced the glass transition temperature, melting temperature and degree of crystallinity. Therefore the heat distortion temperature cannot be improved by this route. [14]

The modification of PLA has been considered as a practical way to enhance certain of its properties. However, improving thermal and mechanical properties without balancing compromising renewability and degradability is not a trivial task. Typically, improved thermomechanical properties are at the expense of renewability/ biodegradability. Hence, reconsideration of the approaches to improve the overall PLA performance is required.

1.1.4 PLA Stereocomplex

1.1.4.1 Background

PLA stereocomplex consists of both enantiomeric poly (L-lactic acid) and poly (D-lactic acid). It has improves general thermal resistance, and mechanical properties when compared to the pure form of either enantiomers. [4] The melting temperature of stereocomplex is 50 °C higher (230 °C) than that of pure PLLA or PDLA (180 °C). [15] The enhancement is due to the unique structure formed between L-lactyl unit and D-lactyl unit. The stereocomplex crystal has PLLA and PDLA chains packed side by side with a triclinic 3_1 helix. Among many parameters affecting stereocomplexation, mixing ratio and molecular weight of PLLA and PDLA are found to be critical. [16] As predicted by Ikada et al.'s study, van der Waals interactions between PLLA and PDLA polymer chains dominate the complexation. [15] To achieve the stereocomplexation, polymers with relatively low molecular weight are required, while polymers with high molecular weights tend to hinder its formation, due to their very low macromolecular mobility. [16] By using melt mixing to form stereocomplex, the threshold of molecular weight for the formation of the stereocomplex is around 6,000 g/mol, in contrast with 40,000 – 400,000 g/mol achievable by solution casting and precipitation, respectively. [16, 17] As Auras et al. described, [4] Strong shear can induce stereocomplexation, by rotating and extending macromolecular chains of PLA and facilitating the enantiomeric sequences.

The structure of PLA stereocomplex has been studied by X-Ray Diffraction. The diffraction patterns are shown in Fig. 1.6. [18]

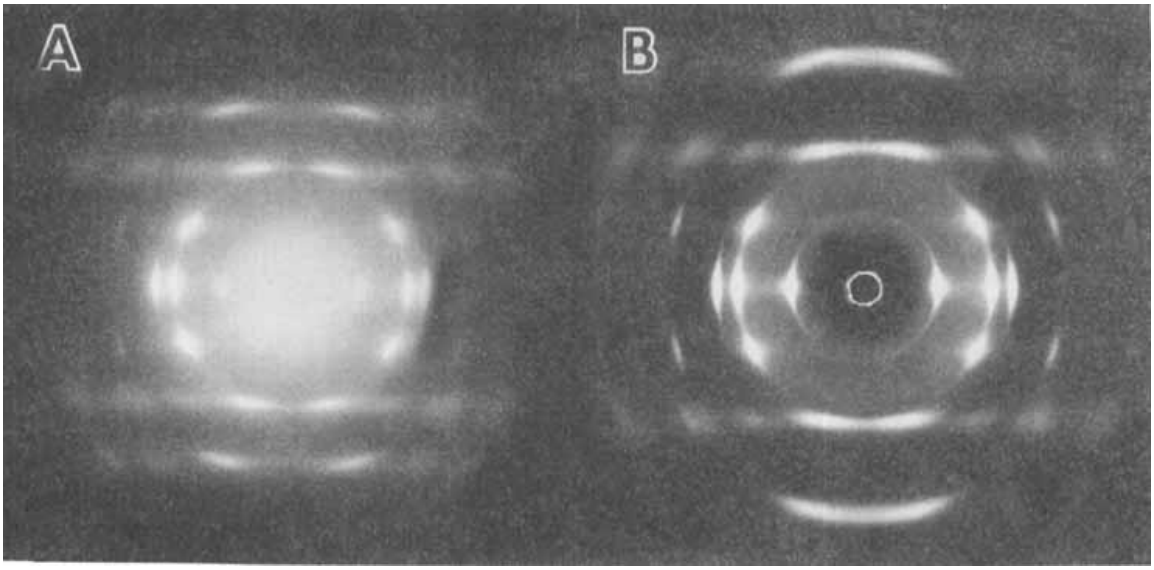


Fig. 1.6 (A) Electron diffraction pattern of a crystalline PLA stereocomplex film, and (B) x-ray fiber pattern. [18]

Okihara et al. have suggested from these patterns that the stereocomplex crystal has a triclinic structure with cell dimensions a=0.916 nm, b=0.916 nm, c=0.870 nm (fiber axis), α=109.2 °, β=109.2 °, γ=109.8 °. [18] Considering the previous study which revealed that in the unit cell, the number of L-units and D-units should be equal, the

PLLA and PDLA stereocomplex is presumed to possess a 3_1 helix in its crystal. [19] Using the conformational parameter equation for polymer helices composed by Miyazawa, the existence of the 3_1 helix has been proved. [20] Fig. 1.7 gives the models of the PLLA helical structure.

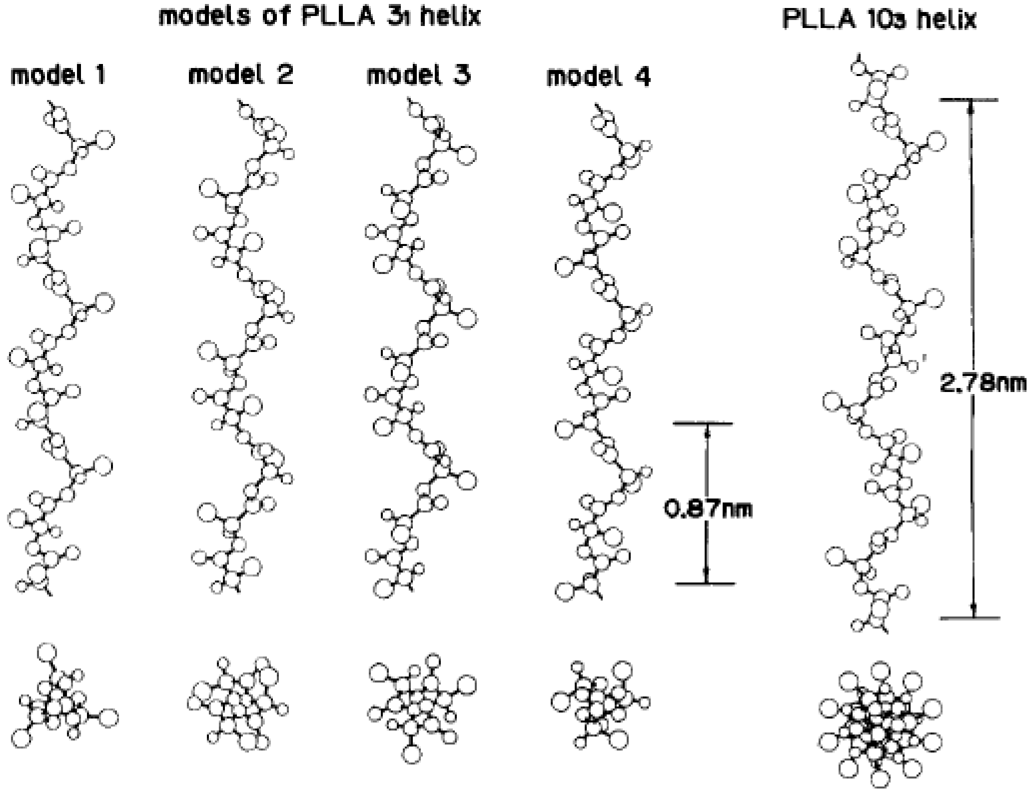


Fig. 1.7 Models of PLLA helix structure. [18]

As shown in Fig. 1.7, the 3_1 helix structure is slightly extended. With the lowest conformational energy, model 1 has been confirmed to be the most stable, among the four different models. [18]

A PLLA chain is left-handed, while a PDLA chain is right-handed, both making up the helical system. When the mixing ratio of left-handed structure and right-handed structure is 1:1, the two form the most densely packed structure. [18] Thus when they are mixed by 1:1 ratio, the stereocomplex formed by rotating both PLLA and PDLA polymer backbones, results in a side-by-side, highly ordered stable 3_1 helix structure. The strong interaction between PLLA and PDLA explains why the stereocomplex has a high melting temperature, as well as better mechanical properties. Fig. 1.8 shows the crystal structure of PLA stereocomplex. [18]

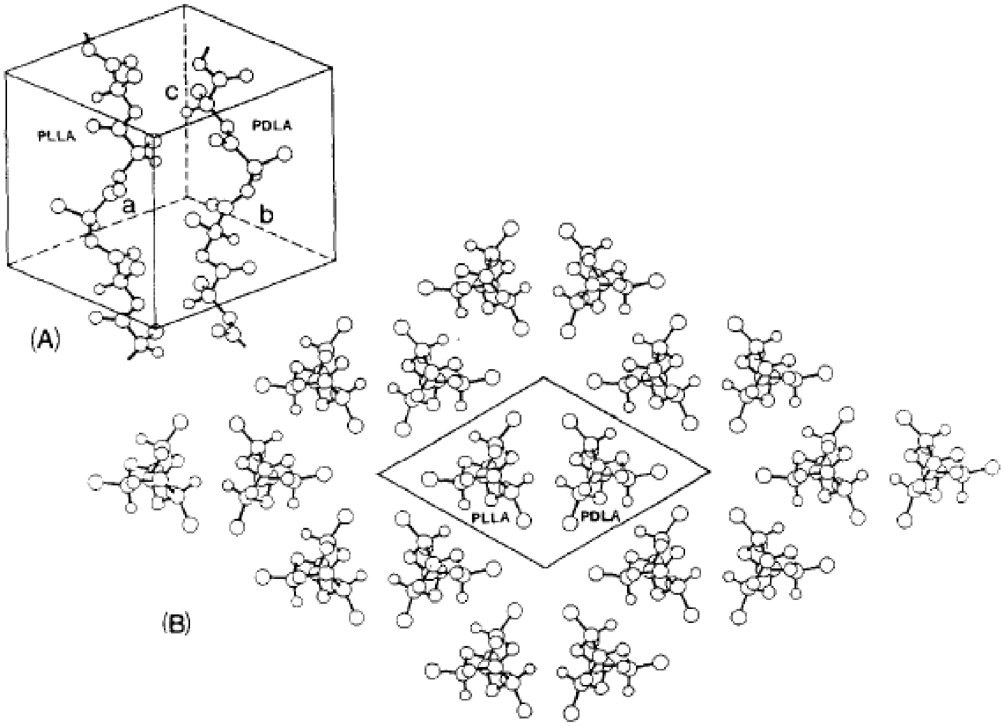


Fig. 1.8 Crystal structure of the PLA stereocomplex. (A) PLLA and PDLA stereocomplex structure model (B) Projected molecular arrangement. [18]

1.1.4.2 Preparation of PLA Stereocomplex

To prepare PLA stereocomplex, the various methods which have been adopted, are listed below.

a. Crystallization from Melt.

Crystallization at a fixed temperature directly from the melt is the most prevalent way to obtain PLA stereocomplex crystal from melt, and it requires equimolar mixture of PLLA and PDLA with low molecular weights. [21]

b. Compression.

Using twin screw extruder, Nam et al. have formed PLA stereocomplex with following temperature profile: 200-230 °C for extruder barrel; die for 220 °C. The screw speed was 200 rpm. [22]

c. Orientation

Reported by Tsuji et al., by hot drawing a large molecular surface area can be created. This increases the possibility of the interaction between PLLA and PDLA polymer chain segments. This method also increases the tensile strength. [23]

d. Solution casting

Solution casting method can be used for with higher molecular weight PLLA and PDLA, but the time given for PLA stereocomplex crystallization must be long enough, otherwise PLLA or PDLA homocrystallites may form. [8]

e. Precipitation

By adding PLLA and PDLA mixture solution into a non-solvent, rapid crystallization of PLA stereocomplex takes place. The low concentration of polymer and the introduction of high shear rate in the non-solvent can induce the formation of PLA stereocomplex over PLLA or PDLA homo- crystallization. [8] Table 1.3 includes methods for preparing PLA stereocomplex.

Table 1.3 PLA stereocomplex preparation methods [8]

Crystallization from melt	1. Crystallization at a fixed temperature from the melt or after melt-quenching
	2. Cooling from the melt or heating after melt-quenching
	3. During polymerization
Solution casting	1. Evaporation the solvent in the mixture solution
Precipitation	1. Precipitation into non-solvent
	2. Precipitation or gel formation at a constant polymer concentration
Drawing or orientation	1. Hot-drawing
Compression	1. Twin screw extruder
	2. After preparation of monolayer film

1.1.4.3.1 Properties

Due to the exceptionally strong interaction taking place via the 3_1 helix structure between PLLA and PDLA, a number of properties of PLA are expected to be improved significantly.

Table 1.4 summarizes the comparison of thermal and mechanical properties between PLLA and PLA stereocomplex.

Table 1.4 Comparison of thermal and mechanical properties between PLLA and PLA stereocomplex [8]

	PLLA	PLA stereocomplex
Tm °C	170-190	220-240
Tg °C	50-65	65-72
ΔHm J/g	93-203	142-155
Density g/cm^3	1.25-1.30	1.21-1.342
Tensile strength MPa	120-2260	880
Young's modulus GPa	6.9-9.8	8.6
Elongation at break %	12-26	30

However, the crystallization process of PLA stereocomplex is affected by various parameters such as mixing ratio, molecular weight of homopolymers, melting temperature etc. Thus, a variety of studies of the crystallization of PLA and PLA stereocomplex have been carried out.

1.2 Crystallization Process

1.2.1 General

Crystallization of polymers involves a series of steps in which polymer chain alignment happens. During these steps, polymer chains fold and form various multilayered, dendritic, spheroidal structures called spherulites. Spherulites are spherically shaped poly-crystalline structures. An example of low density polyethylene spherulites can be seen in Fig. 1.9. [24]

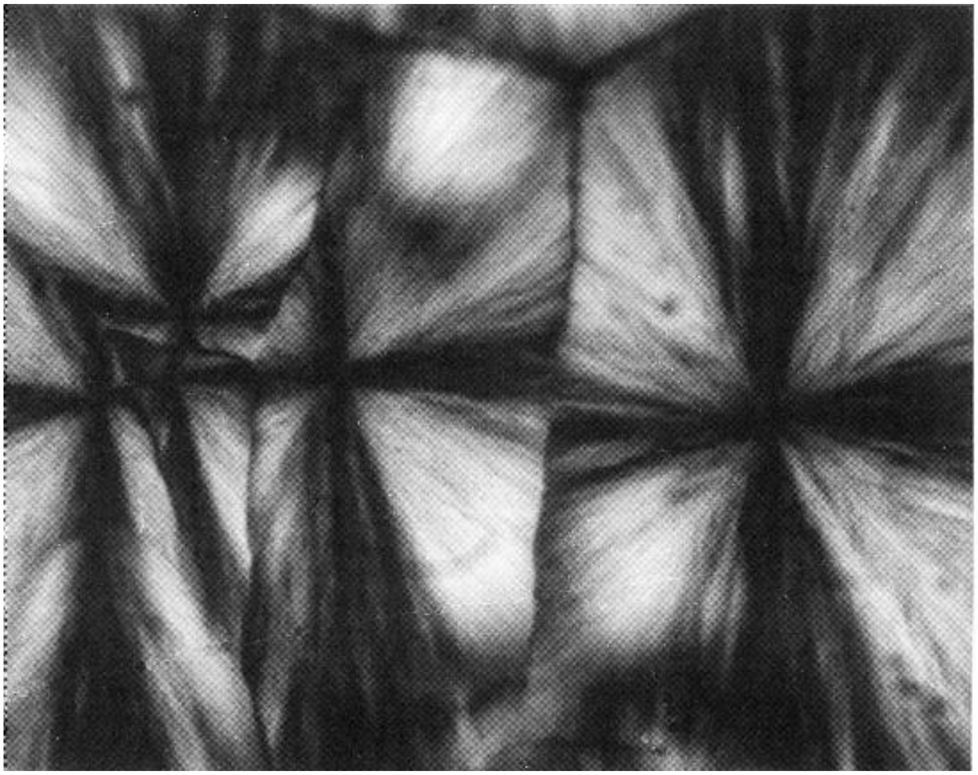


Fig. 1.9 Low density polyethylene spherulites, observed with crossed polarizers. [24]

Using a polarizer, spherulites can be easily observed, with a recognizable extinction cross, which is called a “Maltese Cross”. [24] There are three commonly used ways to obtain polymer crystalline structures:

1. Cooling from the melt
2. Solvent evaporation
3. During and following mechanical stretching.

With different crystalline structures or degrees of crystallization, polymers possess distinct properties including:

1. Thermal properties such as glass transition temperature, melting temperature and heat deflection temperature;

2. Mechanical properties such as brittleness, tensile strength, impact strength and elasticity;

3. Optical properties such as opacity and transparency;

4. Chemical properties.

1.2.2 Crystallization Mechanisms

To have a better understanding of the methods adopted in this study, different crystallization mechanisms are reviewed. Here, it is worth noting that not all polymers can crystallize. Whether a polymer can crystallize depends on the chain structure of polymer, among other things. Statistically, isotactic and syndiotactic polymers tend to be more crystallizable over atactic polymers, because of the sterical hindrance reasons.

Crystallization process is a series of procedures to create a more ordered, aligned polymer chain arrangement via actions like folding and rotating. It involves two major steps: nucleation and crystal growth.

1.2.2.1 Nucleation

In the melt, pure polymer crystal nuclei may form via fluctuations in local order. [25] This is commonly below the nominal T_m of the polymers with supercooled conditions applied. Nucleation usually takes place on suspended particles, bubbles, dirt, or the polymer itself. All the above are essentially nucleation sites. Occurring on preferential nucleation sites, this kind of nucleation is called heterogeneous nucleation, while it is homogeneous nucleation with no preferred nucleation sites. [26]

Homogeneous nucleation is generally more difficult to occur. The creation of nucleus takes place within the uniform substance, due to the thermal motion of the molecules or chain segments. The driving force of nucleation comes from supersaturation, which is achieved via supercooling. This supersaturation creates a free energy change ΔG_v, which will be then be used for creating a new interface, within uniformed molecules. The Gibbs free energy theory states that, when ΔG_v is negative, nucleation will occur, spontaneously. [27]

In comparison with homogeneous nucleation, heterogeneous nucleation takes place much more easily. In the presence of impurities or phase boundaries like "dirt" (particulate solid), container wall or catalyst particulates, heterogeneous nucleation will occur at higher rates and at higher temperatures, since such sites possess low surface energy. Those impurities can lower the surface energy, and consequently reduce the free energy barrier to promote nucleation. [27] This can be found in Fig. 1.10.

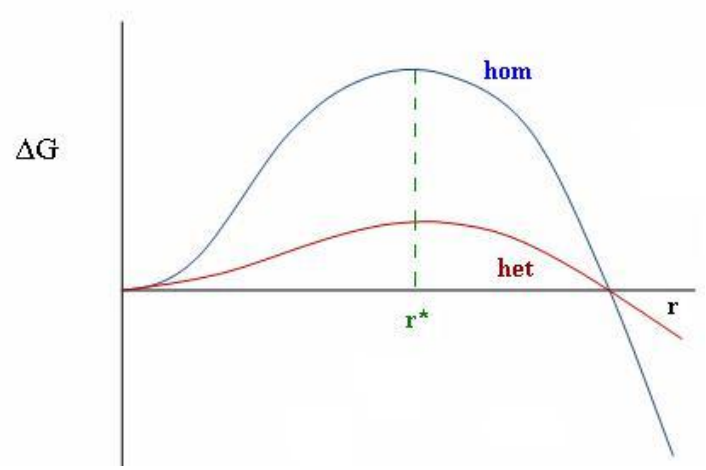


Fig. 1.10 Comparison of the energy barriers of homogeneous nucleation and heterogeneous nucleation. [27]

1.2.2.2 Crystallization from the Melt

Below the polymer melting temperature T_m and above its glass transition temperature T_g, the crystal growth takes place. When the temperature is higher than T_m, the free energy of the polymer chains is not favorable enough to form the ordered arrangement between chains. When the temperature is lower than T_g, polymer chains cannot move due to their frozen segments immobility. [28] As crystallization proceeds, the first ordered structure created is the single crystal, which then may grow into sheaf-like structures that exist in the intermediate stage of the spherulitic growth. With the lamellae growing on either side of the center of the sheaf-like structure, it progressively fans out and forms dendritic branches to create a mature/large spherulite. The entire process is shown in Fig. 1.11. [24]

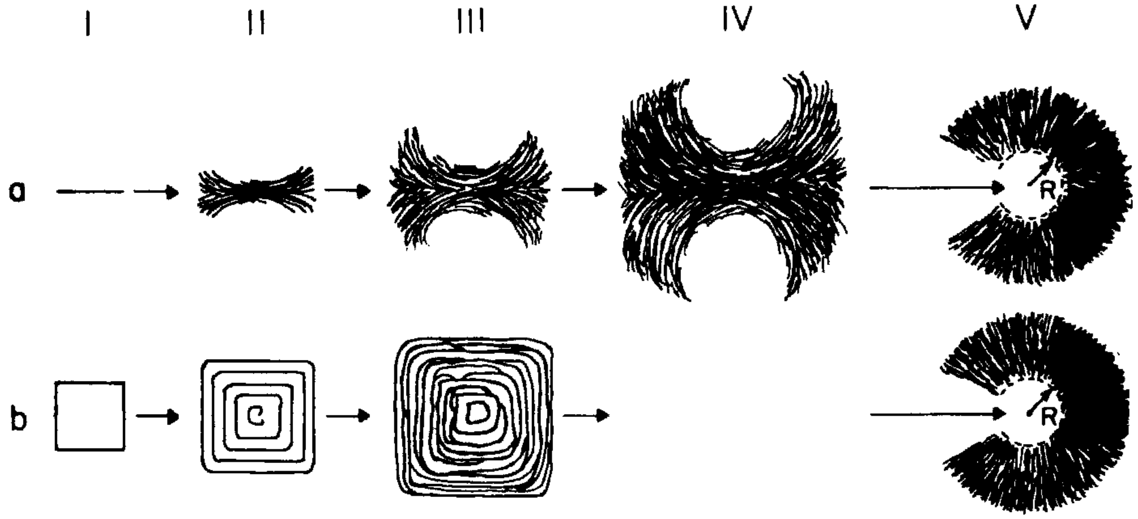


Fig. 1.11 The development of a spherulite, with edge-on and flat-on views in row a and row b, respectively. [24]

1.2.2.3 Crystallization from Solution

Other than crystallization from melt, polymers can form crystals in solution upon the evaporation of solvent. Within dilute solutions, polymer chains tend to disconnect from each other as separate polymer coils. The evaporation of solvent increases the concentration thus more and more interactions between polymer chains take place, which induce the crystallization in solution. This may create the opportunity to obtain the highest degree of crystallinity. [29]

1.2.2.4 Degree of Crystallinity

Degree of crystallinity describes the extent of orderly arranged molecules in polymers.[28] In the study of glass transition dynamics and structural relaxation of PLLA, Mano et al showed a useful and simple way to calculate the degree of crystallinity. [30] By integrating the melt endotherm during melting, the degree of crystallinity can be determined by equation [28]:

$$\boldsymbol{X_c} = {}^{\Delta \boldsymbol{H_f}}\!\big/_{\Delta \boldsymbol{H_f^0}} \tag{1-1}$$

where ΔH_f is the melting enthalpy and ΔH_f^0 is the heat of melting of a single polymer crystal at equilibrium melting temperature.

1.2.2.5 Isothermal Crystallization of Polymer

Using the DSC the kinetics of crystallization can be studied during isothermal heating of samples. The isothermal crystallization kinetics are analyzed with the Avrami theory, described by the Avrami equation:

$$X_c = \exp(-kt^n) \tag{1-2}$$

where X_c is the degree of crystallinity, k is the crystallization rate constant, t is the time, and n is the Avrami exponent. From the equation, the overall crystallization growth rate of polymer, as well as qualitative explanation of nucleation and crystallization behavior can be attained from n and k. Transformation of the equation (1-2) into linear form leads to:

$$\mathrm{lg}[-ln[1 - X_c]] = lgk + nlgt \tag{1-3}$$

by plotting $lg[-ln(1-X_c)]$ versus lgt, n can be obtained as the slope, and lgk as the intercept.

Thus, from n and k attained, we can compare the growth rate of same polymer upon different crystallization conditions, or determine the crystallization kinetics of different polymers under the same conditions. [25]

1.2.2.6 Non-isothermal Crystallization of Polymer

Commonly, the crystallization studies are carried out under assumed idealized conditions, in which external conditions like pressure, temperature, are constant. Under these circumstances, the theoretical analysis is easier to be conducted and most problems connected to cooling rates and thermal gradients within the specimens are avoided. In reality, however, the external conditions change continuously. This leaves the crystallization under varied temperature and some other conditions harder to control. Yet, practically speaking, the study of crystallization in a continuously changing environment is of greater significance, due to the existence of non-isothermal conditions in industrial processes, which are most often non-isothermal. [31]

Non-isothermal crystallization is broadly used to intuitively compare the parameters such as crystallization rate and melting enthalpy. It can reflect the dissimilarities in crystallization process between different polymers or polymer blended with different additives. During non-isothermal study, the controllable factors that can affect general crystallization process include: a. distinct cooling/heating rate; b. different thermal histories; c. different gas atmosphere, etc.

1.2.3 PLA Crystallization

1.2.3.1 PLA Homocrystallization

In general, the discussion above can give us a brief description and understanding of crystallization; as well as provide theoretical bases for studying the crystallization of PLA. In fact, to have a thorough understanding of PLA crystallization, many parameters have to be taken account, which include molecular weight, contents of different isomer, crystallization conditions, thermal history, processing method, optical purity, etc.

Regarding characterization methods, polarized optical microscopy (POM) and DSC are two simple and effective methods commonly used to study nucleation density, spherulite growth rate, degree of crystallinity, glass transition temperature and melting temperature. Using POM, the crystal growth rate (G) can be obtained from the slope of the spherulite radius – time plot, while the induction time can be determined via extrapolation of the plot to zero-radius. [32] With DSC, the isothermal and non-isothermal studies can be conducted.

It is well known that the improvement on degree of crystallinity can noticeably change the mechanical properties, as well as heat deflection temperature. [33] Ahmed et al. investigated the effect of molecular weight and different isomer contents on thermal properties and degree of crystallinity of PLLA. Synthesized from L-lactide monomer using tin-catalyzed ring-opening polymerization, the PLLA samples had molecular weight range of 4,700-150,000 g/mol. From DSC non-isothermal studies, it was found that the degree of crystallinity increased 7-fold, from 8.26% to 56.67%. [34] Likewise, Mano et al. determined that the degree of crystallinity of PLLA of 58,000 g/mol molecular weight is between 24-28%. [30] This result is in fair agreement with Ahmed et al.'s study. Similarly, Bigg has reported for PDLLA of molecular weight lower than 300,000 g/mol, that the degree of crystallinity could reach 30-50%, while there was no crystallization exotherm or melting endotherm observed on PDLLA of 400,000 g/mol molecular weight. [35]

By adopting different processing methods, including hot-drawing, extrusion and injection, the impacts from external stress on degree of crystallinity and other thermal properties of PLA, have been studied. [36, 37] The key parameter in hot-drawing is the draw ratio (DR), which indicates the speed ratio of the first and second roll. By controlling the DR, various levels of stress can be achieved. [37] Table 1.5 shows the selected data obtained from cold crystallization by DSC investigation.

Table 1.5 Selected data of thermal properties of processed PLA [36, 37]

PLA Processing Method	Tg(°C)	Tm(°C)	Xc (%)
HD, DR=200:400	61	153	10
HD, DR=200:600	62	145	16
HD, DR=150:450	65	147	17
HD, DR=150:600	67	146	41
Virgin	N/A	154	30
Extruded	N/A	156	33
Injected	N/A	165	35

Even though the conformations of the materials processed by hot-drawing and extrusion or injection are different, it shows that strong external stress can orient polymers and change their degree of crystallinity, as well as the melting temperature. [36,37] In addition, from Pantani et al.'s study, the kinetic constants obtained from isothermal crystallization data showed an increase for processed PLA over virgin PLA.[37]

Furthermore, studies of morphological influences on PLA crystallization by using modulated temperature DSC (MTDSC) have been carried out. [30, 38] MTDSC allows to separate the enthalpic relaxation and glass transition, and to avoid errors brought by the instruments. With this powerful tool, accurate quantitative thermal analysis was carried out, to determine the mobile amorphous fraction and rigid-amorphous fraction. [38]

1.2.3.2 PLA Crystallization with Nucleating Agents

Generally, the crystallization rate of PLA is relatively low. The complete crystallization process can take months. Previous efforts to improve crystallization kinetics have been made. The use of nucleating agents appears to be the most viable way. With heterogeneous nucleation sites, the nucleation induction time can be reduced without requiring high driving force. Thus the overall crystallization rate can be increased.

Different types of nucleating agents can be categorized as mineral, organic and mineral-organic. [32] The use of talc, a popular inorganic nucleating agent, as well as the PLA stereocomplex on PLA crystallization, are discussed in some detail:

a. Talc as nucleating agent

Talc is among the most well-known one nucleating agents for PLA because of its efficiency on enhancing PLA crystallization and mechanical properties as well as being of low cost. [22, 39, 40, 41, 42, 43] For example, Urayama found that with the addition of talc, the crystallization of PLLA began at 170 °C, which was 60 °C higher than that of the pure polymer. [40] Also in Nam et al.'s study, improvements on impact strength and heat distortion temperature were observed. In addition, crystallization half-time ($t_{1/2}$) decreased 10-fold with talc content. [22]

b. PLA stereocomplex as nucleating agent

Given the strong interaction between PLLA and PDLA, the stereocomplex itself could be considered as a potential nucleating agent, because of the highly similar chemical composition to PLLA. In Brochu et al.'s study, it was found that PLLA homopolymer could crystallize epitaxially on the stereocomplex surface when the SC exists. Other than forming new nuclei and new crystallization sites, the direct epitaxial crystallization will expedite the PLLA crystallization process. This result clearly showed that the stereocomplex can be used as a nucleating agent for PLLA crystallization. [44]

Yamane et al., Narita et al. and Tsuji et al. have studied the addition of PDLA on enhancing PLLA crystallization. In their studies, the nucleating effect was influenced by different PLLA/PDLA blending ratios and molecular weight. [45, 46, 47] Results showed an overall improving on PLLA crystallization. With increasing PDLA (M_w = 50,000 g/mol) content, the nucleation effect was strengthened. This was confirmed by the much earlier appearance of PLLA homocrystallization peak compare to that of neat PLLA, suggesting a nucleating effect brought by SC. [46] The spherulitic growth rate increased with PDLA content, as observed by POM. [45] Tsuji et al. found that the spherulite density increased with PDLA content, and the crystallization induction time decreased with PDLA contents. [47]

To quantitatively depict the enhancement brought by PDLA, Schmidt et al. and Anderson et al. studied the nucleation efficiency of the PLA stereocomplex, as nucleating agent. [25, 43] The concept of nucleation efficiency was first proposed in Fillon et al.'s study [48], then further explained by Schmidt et al.. [25] The nucleation efficiency scale can be expressed by following equation:

$$NE = \left(\frac{T_c - T_c^{min}}{T_c^{max} - T_c^{min}}\right) \times 100 \tag{1-4}$$

$\boldsymbol{T_c^{min}}$ is the crystallization temperature obtained when the plain PLLA is cooled from the amorphous state, without PDLA. $\boldsymbol{T_c^{max}}$ is the crystallization temperature when the crystallized pure PLLA is partially melted and self-nucleated with the remaining crystals, with no incorporation of PDLA. T_c is the crystallization obtained from blends containing different PDLA content.

As reported by Schmidt and Hillmyer, with same amount PDLA and talc blended with PLLA, respectively, the nucleation efficiency of PDLA blended system could be double as that of talc. [25] A similar tendency was later confirmed by Anderson et al.. [43] Tables 1.6 and 1.7 show the results of nucleation efficiency from two studies.

Table 1.6 Selected results from Schmidt et al.'s study [25]

Additive	Additive Content (wt%)	Tc (℃)	NE (%)
None	0	106.3	0
PDLA	0.25	113	13
PDLA	0.5	125.3	37
PDLA	1	124.4	36
PDLA	4	132.2	51
PDLA	10	138	63
PDLA	15	139.8	66
Talc	6	122	32

Table 1.7 Selected results from Anderson et al.'s study [43]

Additive	Additive Content (wt%)	Tc (℃)	NE (%)
PDLA (5,800 g/mol)	0.5	130	13
PDLA (5,800 g/mol)	3	137	36
PDLA (14,000 g/mol)	0.5	136	83
PDLA (14,000 g/mol)	3	141	94
PDLA (48,000 g/mol)	0.5	130	66
PDLA (48,000 g/mol)	3	135	81
Talc	6	123	50

1.3 Objectives of the Thesis Work

The aim of this work is to study the nucleation effect of PLLA/PDLA stereocomplex on the PLLA crystallization process. With PDLA molecular weight as 340,000g/mol, which is higher than that of used in early studies, several samples with different PDLA blending ratios were being prepared to characterize the nucleating effect on PLLA crystallization, brought by different PDLA content. With DSC analysis and hot stage POM, samples were studied qualitatively and quantitatively. In non-isothermal DSC analysis, the glass transition temperature, melting temperature, crystallization temperatures, degree of crystallinity were determined. In isothermal DSC analysis, the crystallization induction time, crystallization half-time, and crystallization enthalpy were determined, and the crystallization kinetic parameters were calculated and compared. In the POM study, observation on nucleation and crystallization growth behavior was visualized, including observation of spherulite density, number, and size, as well as estimation of the overall spherulite lateral growth rates. Moreover, thermogravimetric analysis (TGA) was used to detect any thermal degradation of the polymers as well as the presence of residual solvent.

CHAPTER 2

EXPERIMENTAL

2.1 Materials Used in the Thesis Work

2.1.1 Poly (lactic acid)

a. Poly (L-lactic acid):

Brand name: PURASORB PL 24;

Grade: GMP;

Molecular weight: 340,000 g/mol;

Density: 1.24 g/cm^{-3} at 25 °C;

Water content: max. 0.5%

b. Poly (D-lactic acid):

Brand name: PURASORB PD 24;

Grade: GMP;

Molecular weight: 340,000 g/mol;

Density: 1.24 g/cm^{-3} at 25 °C;

Water content: max. 0.5%

Polymers in pellets form were sent by Purac® Biomaterials – The Netherlands.

2.1.2 Solvents

Dichloromethane

Grade: anhydrous

Impurities: max. 0.001% water

Boiling point: 39.8-40 °C

Density: 1.325 g/mL at 25 °C

Solvent was supplied by Sigma Aldrich.

2.2 Characterization Methods

2.2.1 Differential Scanning Calorimetry (DSC)

DSC Q100 from TA universal Instruments was used to carry out thermal properties tests. Isothermal and non-isothermal experiments were conducted using several different heating protocols.

a. To determine the glass transition temperature, melting temperature, crystallization temperatures and degree of crystallinity, several tailored non-isothermal programs were proposed.
b. In isothermal crystallization studies, the crystallization induction time, crystallization half-time, and crystallization enthalpy were determined under different isothermal crystallization temperatures.

2.2.2 Hot Stage Polarized Optical Microscope

A polarized optical microscope (Carl Zeiss Universal Research Microscope) and a hot stage (Mettler FP90) were used to study crystal growth behavior upon heating and cooling.

The spherulitic morphology of samples containing different PDLA content were observed and described.

2.2.3 Thermogravimetric Analysis

Thermogravimetric Analyzer TGA7 from Perkin Elmer Inc. was used in this work. The non-isothermal experiments were carried out by heating the samples to 400 °C at 40 °C/min. The isothermal experiments were performed by isothermally keeping the samples at 240 °C for 20 min. The thermal degradation of PLLA and the amount of residue solvent were determined.

2.3 Sample Preparation

Samples of PLLA/PLDA blends containing six different PDLA contents, 0.3, 0.5, 1, 3, 5, 10, and 15 wt% were prepared by solution casting method. First, samples were dissolved in methylene chloride while rigorously stirring for 1 hour. Using a volumetric pipette, the solutions were mixed precisely according to given blending ratios. To cast the films, the blended solution was poured onto aluminum pans with diameter of 50 mm. The pans containing the casted solutions were dried for 4 hours in the hood covered with beaker with only a thin slit for solvent evaporation. The purpose of this step was to keep solvent evaporation at lower rate, so that no bubbles would be produced reducing the homogeneity of the casted films. When most of the solvent was removed, the pans were transferred into vacuum at 90 °C, to remove the residual solvent. Samples for optical microscopy were obtained by cutting thin pieces with dimensions of about 4 mm×8 mm, from the thoroughly dried-out cast films.

2.4 Results

2.4.1 DSC Non-isothermal Analysis

2.4.1.1 PLLA T_c, T_g and T_m Determination

PLLA samples were rapidly heated (100 °C/min) from 25 °C to 200 °C, and were held for 3 min to completely melt PLLA and erase any prior thermal history. Next, the samples were then cooled (5 °C/min) from 200 °C to 40 °C, allowing PLLA homopolymer to crystallize. The blends were again heated from 40 °C to 200 °C, at 10 °C/min, to determine the glass transition and melting temperatures. The glass transition temperature was obtained as the temperature at lower limit of glass transition. The crystallization and melting temperatures were taken as the peaks of the crystallization exotherm and melting endotherm respectively.

During the 1st cooling process, the T_c of PLLA was 103.56 °C, as seen in Fig. 2.1.

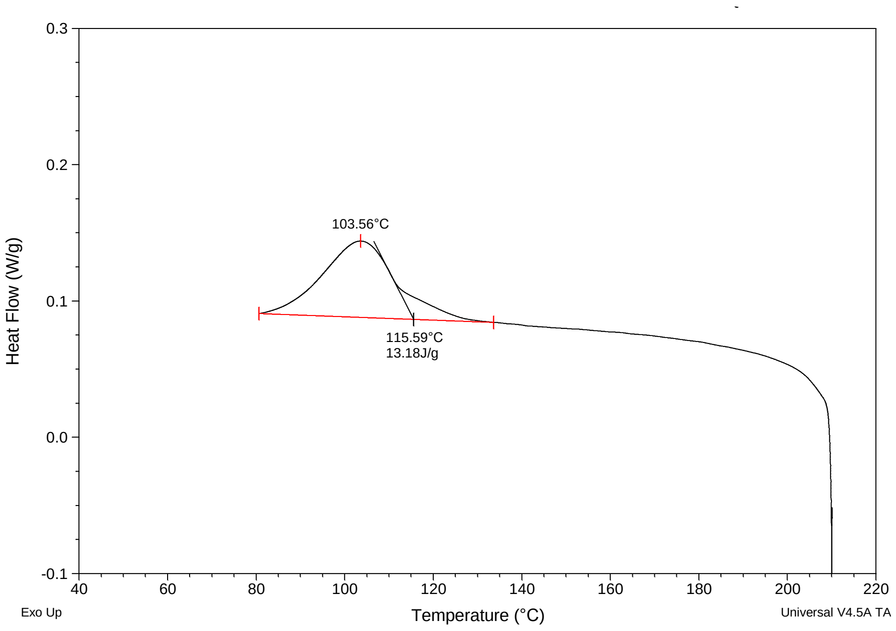


Fig. 2.1 PLLA crystallization temperature and enthalpy upon 5 °C/min cooling.

During 2nd heating, T_g and T_m of PLLA were found to be 62.4 °C and 177.52 °C, respectively. The results of T_g and T_m are given in Fig. 2.2 and Fig. 2.3, respectively.

The T_c, T_g and T_m obtained were in agreement with the literature. [4, 8]

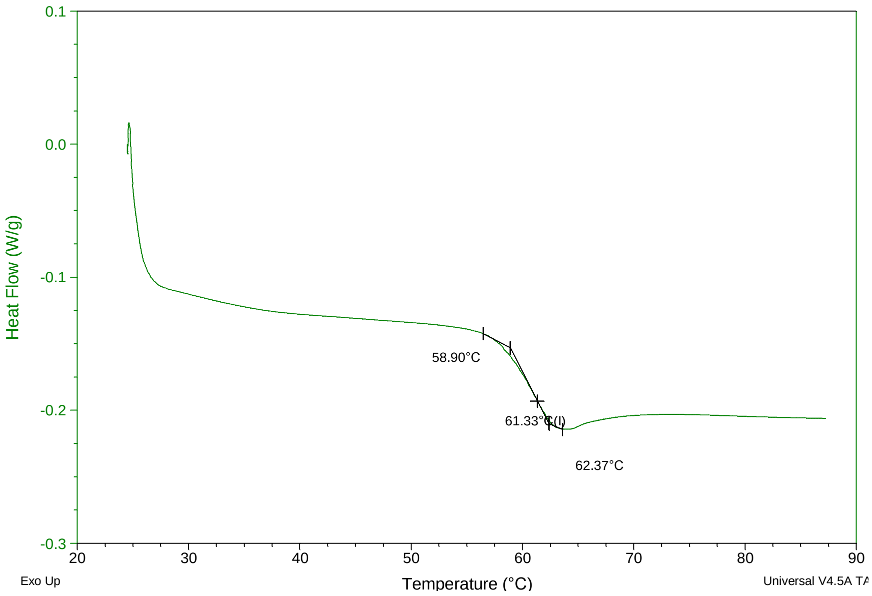


Fig. 2.2 Glass transition temperature of PLLA homopolymer.

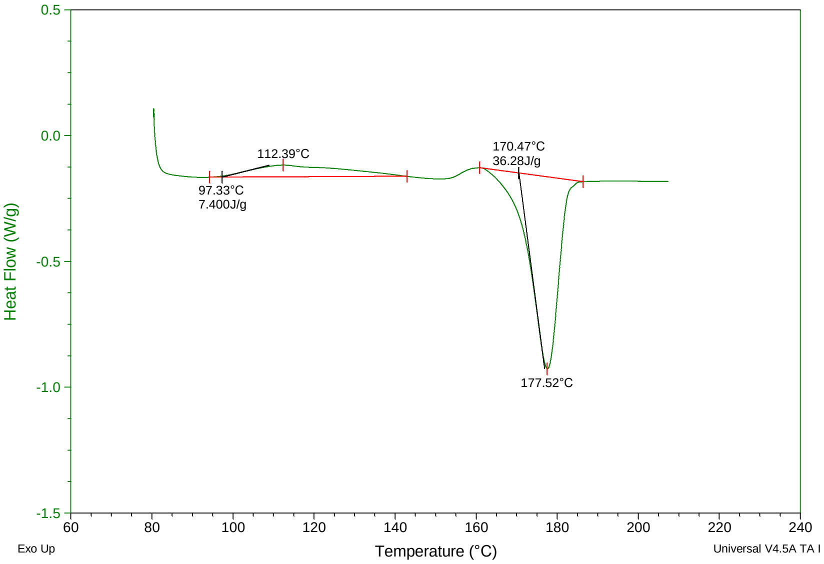


Fig. 2.3 Melting temperature of PLLA homopolymer.

During the 2nd heating to 200 °C, as shown in Fig. 2.3, in addition to melting, an exothermic peak was detected at 112.39 °C. This peak is related to the recrystallization of PLLA that maybe due to the insufficient amount of crystals formed during the 1st cooling from 200 °C at 5 °C/min. From the melting enthalpy of 100% crystalline PLLA ($\Delta H_m{}^{\infty}{}_{PLLA}$ = 94 J/g), [43] the degree of crystallinity (X_c) of PLLA homopolymer (Table 2.1) can be calculated using the following equation

$$X_c = 100 \times \Delta H_{mPLLA} / \Delta H_m{}^{\infty}{}_{PLLA} \qquad (2\text{-}1)$$

Table 2.1 Degree of crystallinity of PLLA homopolymer

$\Delta H_m{}^{\infty}{}_{PLLA}$ (PLLA with 100% degree of crystallinity) (J/g)	ΔH_m (J/g)	X_c
94	36.28	39.18%

Here, ΔH_m, is the actual melting enthalpy of PLLA homopolymer obtained during 2nd heating, and X_c is the degree of crystallinity.

Similarly, the T_c, T_g and T_m of pure PDLA is given in Fig. 2.4 and Fig. 2.5, respectively.

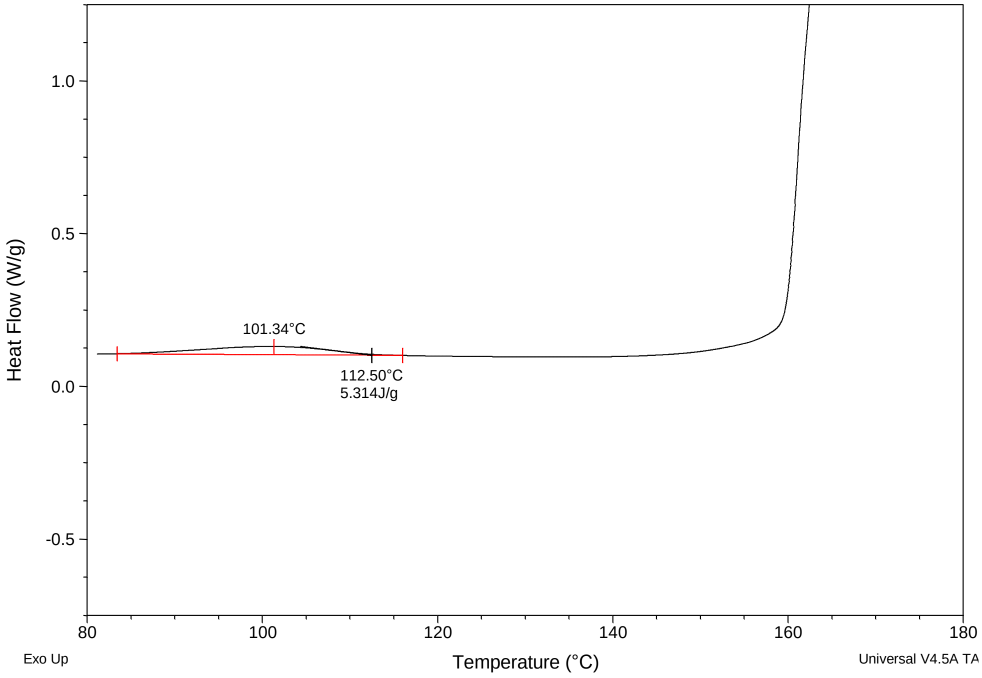


Fig. 2.4 Crystallization temperature of PDLA homopolymer.

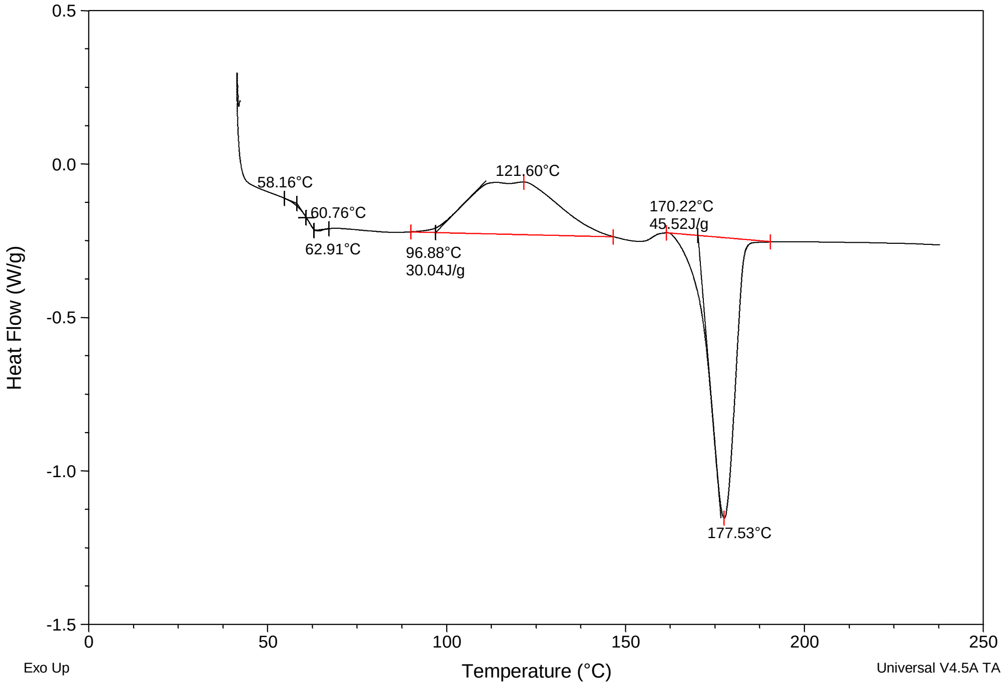


Fig. 2.5 Glass transition temperature and melting temperature of PDLA homopolymer.

As shown in Fig. 2.4 and Fig. 2.5, the T_c, T_g and T_m of PDLA are almost identical to that of PLLA. Also, other than a melting peak, there was no other peak found at temperature appeared above 177 °C, suggesting PDLA itself does not have a greater tendency to crystallize. Thus, the nucleating effect, if it exists, is solely provided by stereocomplex formed during crystallization.

2.4.1.2 PLLA/PDLA Blends T_c, T_g and T_m Determination

a. PLLA/PDLA blends T_m determination

To determine the melting temperature of PLLA/PDLA stereocomplex, blends containing 0.3-30 wt% PDLA were rapidly heated (100 °C/min) to 230 °C and held for 3 min to completely melt the blends and to erase the thermal history. Then samples were quenched (100 °C/min) from 230 °C to 160 °C, and then cooled (5 °C/min) to 80 °C, allowing both stereocomplex and homopolymer to crystallize. Then the blends were heated to 190 °C at 100 °C/min and held there for 3 min, to melt PLLA but leave the SC intact (assuming it was formed in the previous step). Next, the samples were cooled from 190 °C to 80 °C at 5 °C/min to crystallize again, with the existence of SC. Finally, the blends were heated to 240 °C at 10 °C/min, to observe the melting endotherms from PLLA homopolymer and stereocomplex.

The DSC analysis results during 1st cooling and 2nd heating are shown in Fig.2.6 and Fig.2.7, respectively.

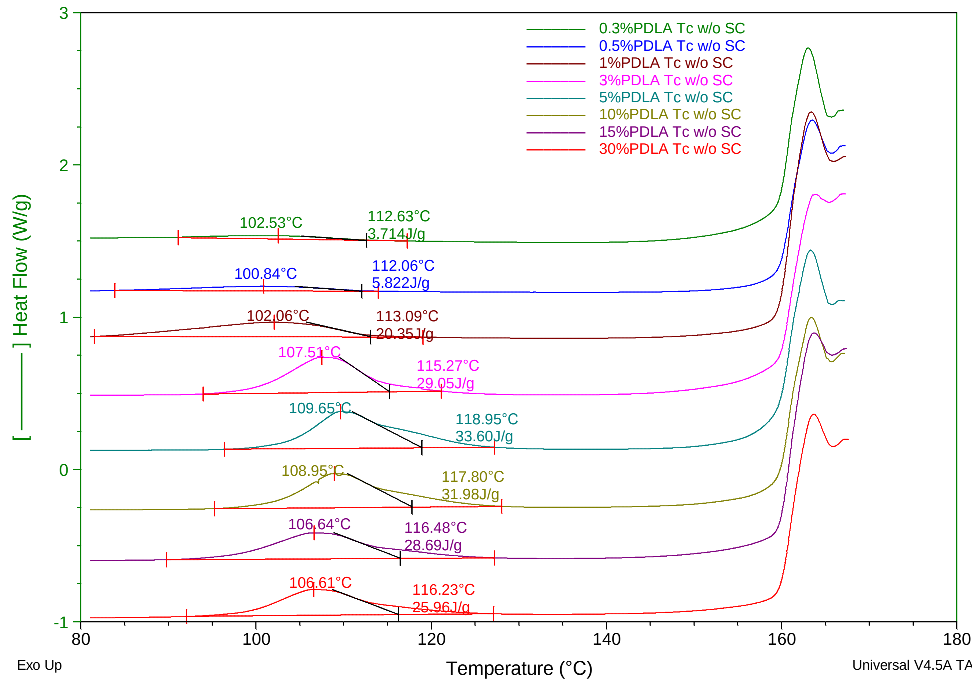


Fig. 2.6 T_c of PLLA with the incorporation of 0.3-30 wt% PDLA without the presence of stereocomplex.

As can be seen in Fig. 2.6, the crystallization enthalpies of the blends with 0.3 and 0.5 wt% PDLA are around 6 times smaller than those of the blends with higher PDLA content, that correspond to the crystallization exotherm of pure PLLA homopolymer. Hence, recrystallization is likely to happen during the 2nd heating at 240 °C. As for the crystallization onset temperature and crystallization temperature (T_c), they were found to be 5 °C lower in blends with 0.3 and 0.5 wt% PDLA, than in blends with higher PDLA content. Considering the absence of SC in the 1st cooling, the impact of additional PDLA was not obvious, on both elevating T_c and the amount of crystals formed during crystallization. However, the minor improvement may because of the greater amount SC formed spontaneously with PLLA crystallization in blends with higher PDLA content.

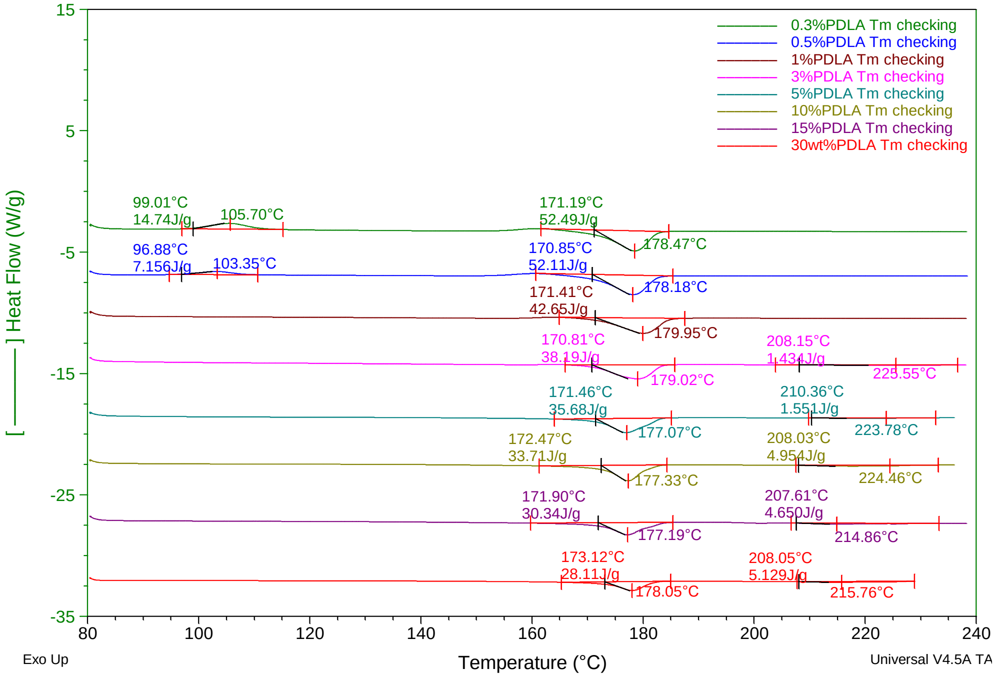


Fig. 2.7 T_m of the PLLA and PLLA/PDLA stereocomplex with the incorporation of 0.3-30 wt% PDLA.

From the results shown in Fig. 2.7, PLLA T_m in samples with different PDLA contents is in the same range as that of pure PLLA (between 177 and 179 °C), suggesting no changes in PLLA crystallization because of the incorporation of PDLA. The stereocomplex melting zone is found below 230 °C in blends with 3, 5, 10, 15 and 30 wt% PDLA, yielding melting peaks in 2 locations: 223-225 °C for blends with 3-10 wt% PDLA; and 214-215 °C for blends with 15 and 30 wt% PDLA. Similarly, this melting behavior has been observed by Tsuji et al. at 223 °C and confirmed the formation of stereocomplex. [16, 21] Anderson et al. and Tsuji et al. found the melting peak at 213 °C, which also reflected the stereocomplex formation. [17, 43] Hence, this result confirmed that the PLLA/PDLA stereocomplex could be successfully prepared, during melt crystallization with 5 °C/min cooling from 160 °C to 80 °C.

Yet within samples with 0.3, 0.5, 1 wt% PDLA, the melting enthalpy of SC was too small to be measured, which is different from that was found in Anderson's study. [43] With 0.5, 1 and 3 wt% PDLA incorporated into PLLA using batch mixer, the T_m of SC was successfully determined, although the melting peak in 0.5 wt% PDLA sample was as low as 0.5 J/g.

Such low melting enthalpy values are close to the "accuracy limit" of DSC. Notwithstanding, the discrepancy may be explained as follows: samples prepared with hot melt-mixing method were mixed more thoroughly, compared to the samples prepared by solution casting method, and the tied-up PLLA/PDLA could have a stronger interaction to form the stereocomplex. Thus even with as low as 0.5 wt% PDLA content, the stereocomplex formed during hot melt-mixing was successfully detected.

Similarly to the determination of the degree of crystallinity (X_c) of pure PLLA homopolymer, from equation (2-1), this PLLA X_c for blended systems was calculated (Table 2.2), while the change of X_c against PDLA content is given in Fig. 2.8. Likewise, the relationship between the amount PDLA incorporated and the SC melting enthalpy is given in Fig. 2.9.

Table 2.2 Degree of crystallinity of PLLA with the incorporation of PDLA

PDLA content (wt%)	PLLA ΔHm (J/g)	PLLA X_c
0.3	52.49	56%
0.5	52.11	56%
1	42.65	46%
3	38.19	42%
5	35.68	40%
10	33.71	40%
15	30.34	38%
30	28.11	43%

In Fig. 2.8, the incorporation of PDLA generally elevated the X_c of PLLA, especially in the samples with 0.3 wt% PDLA, giving X_c of 55%, compared to 39% in pure PLLA. With increasing amount of PDLA incorporated, the X_c of PLLA decreased. In samples containing more than 5 wt% PDLA, X_c reached a plateau around 40%, which is of the same order as that of pure PLLA, suggesting no further improvement on degree of crystallinity brought by high contents of PDLA.

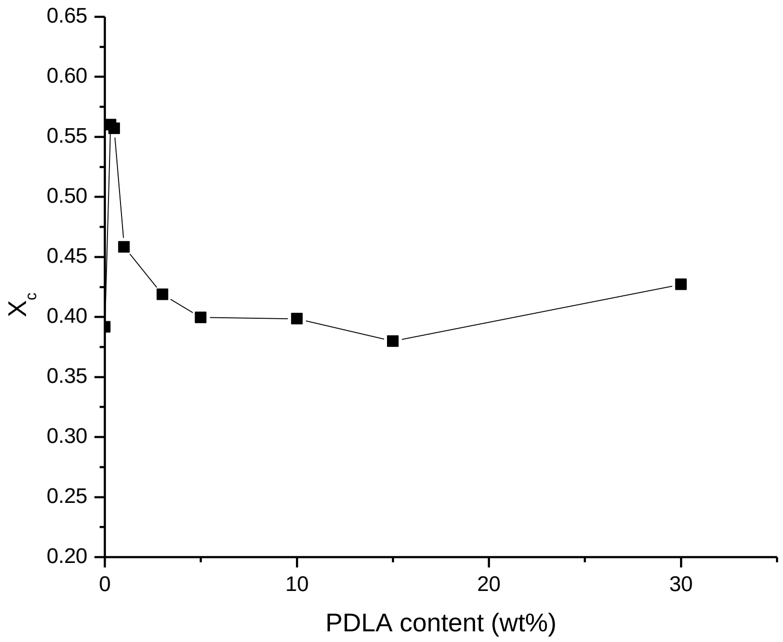


Fig. 2.8 PDLA contents as a function of PLLA degree of crystallinity.

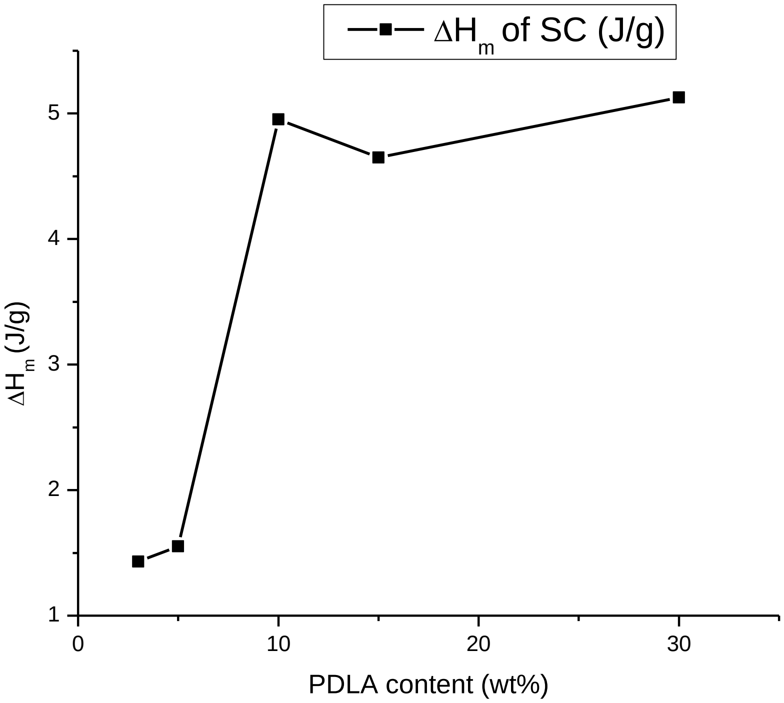


Fig. 2.9 PDLA contents as a function of the SC melting enthalpy.

Shown in Fig. 2.9, with increasing the amount of PDLA added, the SC melting enthalpy increased five times from 0.8576 to 4.954 J/g. A plateau on stereocomplex melting enthalpy was found in blends incorporated with more than 10wt% PDLA, inferring the amount of SC formed during melt crystallization might have reached the upper limit. This phenomenon has not been reported in the literature before, but it could explain the leveling off in PLLA melting enthalpy with more than 5 wt% PDLA. The same amount of SC would provide the same amount of crystallization sites, having the same enhancement on PLLA crystallization, and causing the same extent of crystallization.

Similarly to what was found in PLLA homopolymer, in samples containing 0.3 and 0.5 wt% PDLA, recrystallization happened between 95 °C and 110 °C. Considering the small crystallization exotherm observed in Fig. 2.6, the insufficient amount of crystals formed during melt crystallization may explain this phenomenon.

Comparing with samples containing 3-15 wt% PDLA, the changes in sample with 30 wt% PDLA was hardly noticed. Thus in further experiments, 30 wt% PDLA sample was not prepared.

b. Determination of PLLA/PDLA blends T_c in the presence of stereocomplex

To find out the crystallization temperature in the presence of SC, and to find out the enhancing effect on elevating T_c brought by the SC, PLLA/PDLA blends containing 0.3-15 wt% PDLA were rapidly heated (100 °C/min) to 230 °C and held for 3 min to completely melt the blends and to erase the thermal history. Then samples were quenched from 230 °C to 160 °C, and then cooled (5 °C/min) to 80 °C, allowing both stereocomplex and homopolymer to crystallize. Then the blends were heated to 190 °C at 100 °C/min and held for 3min, to melt PLLA while leaving the SC intact in the system. Finally the samples were cooled from 190 °C to 80 °C at 5 °C/min to determine the T_c in the presence of SC.

To prove that by holding samples at 190 °C for 3 min, pure PLLA can be completely melted while SC can be left intact, following steps are performed: sample containing 15 wt% PDLA was rapidly heated (100 °C/min) to 230 °C and held for 3 min to completely melt the blends and to erase the thermal history. Next, the sample was quenched from 230 °C to 160 °C, and then cooled (5 °C/min) to 80 °C, allowing both stereocomplex and homopolymer to crystallize. After that, the blend was heated to 190 °C at 100 °C/min and held for 3 min, to melt PLLA, and followed by quenching from 190 °C to 145 °C at 100 °C/min. Assume this step can prevent the PLLA crystallization. Finally the sample was heated to 240 °C at 10 °C/min, to check the SC melting exotherm. The DSC curve is given in Fig. 2.10.

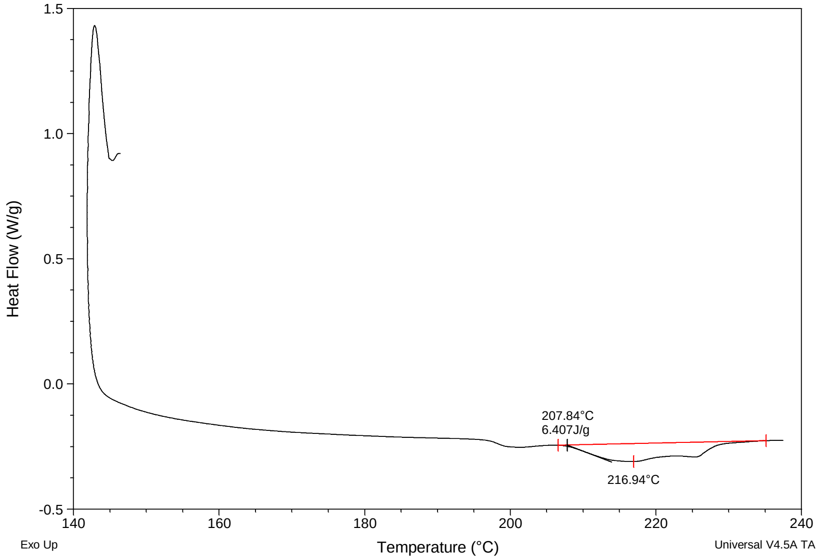


Fig. 2.10 DSC curve of the melting of stereocomplex, without PLLA crystallites.

The absence of PLLA melting peak in Fig. 2.10 indicates that, by holding the samples at 190 °C for 3 min, PLLA crystallites can be completely melted. This proves that other than SC, there is no nucleating agent existing in the blending system.

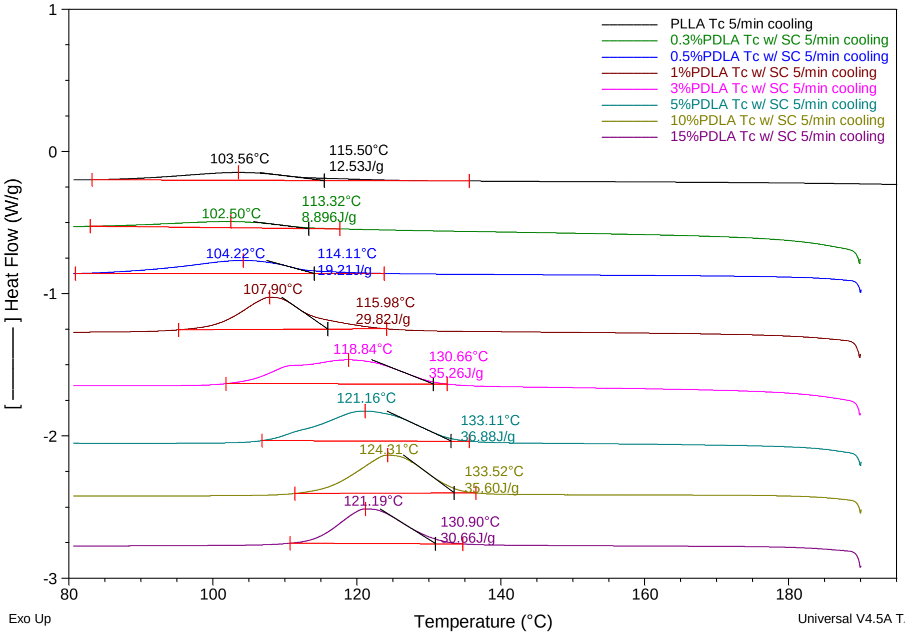


Fig. 2.11 DSC thermogram of PLLA in the presence of the stereocomplex, with 5 °C/min cooling rate.

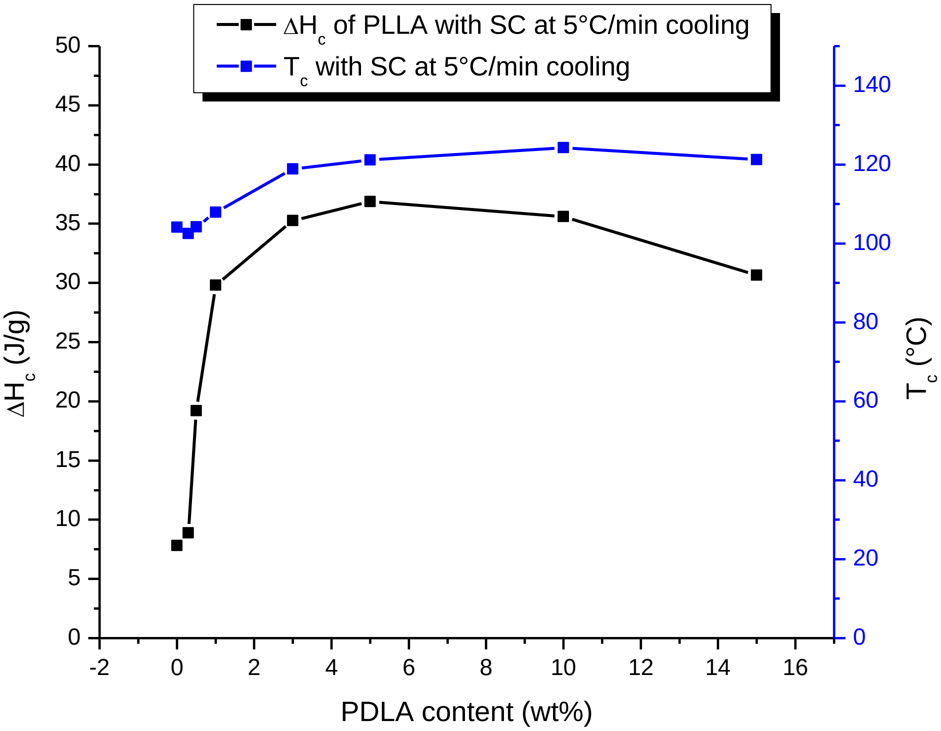
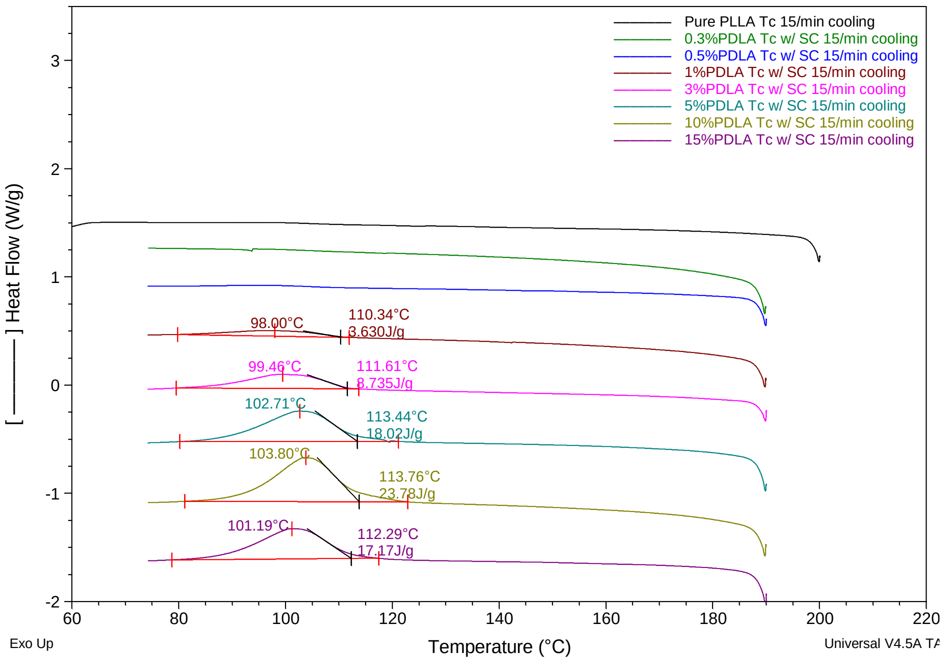


Fig. 2.12 PDLA contents as a function of PLLA crystallization enthalpy and T_c, upon 5°C/min cooling.

Fig. 2.11 shows the thermogram of T_c obtained from pure PLLA and blends containing 0.3-15 wt% PDLA during the final cooling process. Given in Fig. 2.12, with the increasing amount of PDLA incorporated, T_c shifts toward higher temperature. In samples containing 3-15 wt% PDLA, T_c increased noticeably by 15-20 °C comparing to T_c of pure PLLA, and the same behavior appears on onset temperature. Likewise, the crystallization enthalpies in 1-15 wt% PDLA blends are around 4-5 times greater than which obtained in pure PLLA sample. The highest T_c was obtained at 124 °C from the sample containing 10 wt% PDLA. The corresponding crystallization enthalpy is 35.60 J/g, which is 5 times greater than that of pure PLLA. These results suggest the existence of stereocomplex leads earlier occurring of PLLA crystallization in contrast with the case in pure PLLA sample, in which there is no stereocomplex. The overall increase on T_c was previously found and ascribed by Brochu et al.: PLLA homopolymer could crystallize epitaxially on the stereocomplex surface when SC exists. Without waiting for the formation of new nuclei and new crystallization sites at high temperature with low supercooling, the easier direct epitaxial crystallization will expedite and prolong the PLLA crystallization process. [44] Then the fact that T_c decreased with the reduction of PDLA content could be explained as follows: The amount of stereocomplex was not enough to initiate detectable extent of PLLA crystallization at high temperature. Thus through DSC analysis, the early appeared crystallization exotherm is only found in samples with greater PDLA content, because of the greater amount of existing stereocomplex causing more PLLA to crystallize epitaxially.

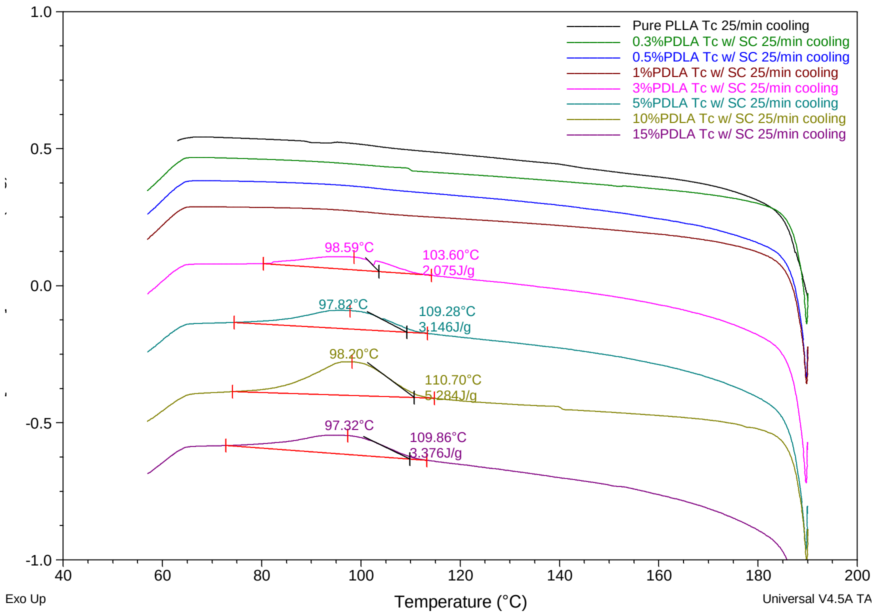
In Fig. 2.12, the leveled-off crystallization exotherms were observed in samples containing more than 3 wt% PDLA. The origin of this phenomenon is the same as the plateau of PLLA melting enthalpy in samples blended with higher PDLA content: During crystallization in the presence of SC, the saturated amount of SC provided equal number of crystallization sites for PLLA to crystallize. Meanwhile, the same cooling rate applied causes the same chain mobility and energy that PLLA polymer chains would have. Thus, the same saturated sites and same fixed chain mobility brings about the same extent of PLLA crystallization, which could be reflected on DSC as the same crystallization exotherms and same range of T_c. The initial increase of PLLA crystallization enthalpy may due to that a small amount of stereocomplex induced the extent of PLLA crystallization. However the increase is not obvious.

One possible way to further examine the enhancing effect on PLLA crystallization brought by the stereocomplex is to apply more rigorous crystallization conditions. Thus two different cooling rates (15 and 25 °C/min) were utilized to induce PLLA/PDLA blends crystallization in the presence of stereocomplex. The intention of this was to emulate the crystallization process prevalently adopted in polymer industry.



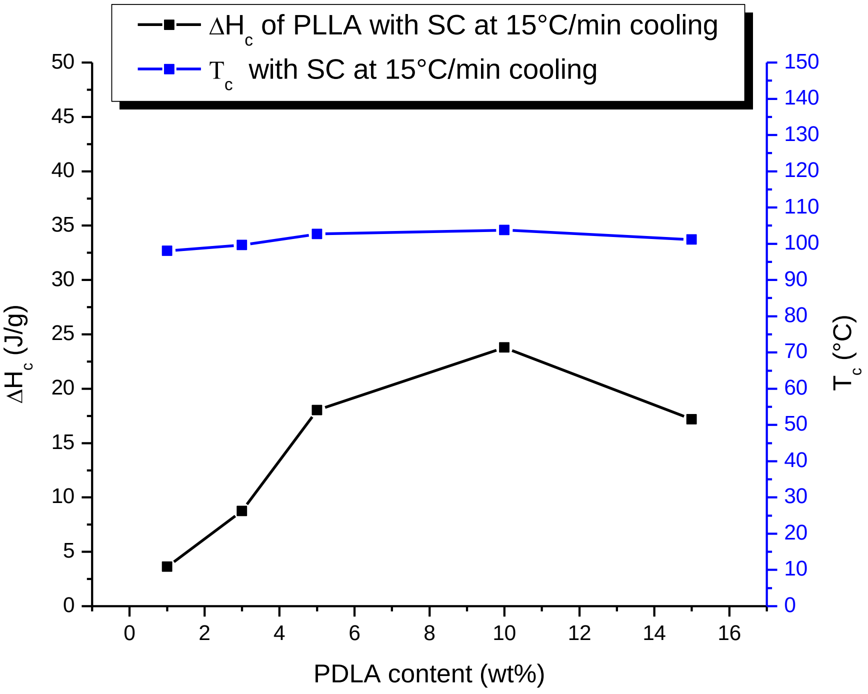
(a)

Fig. 2.13 DSC thermogram of T_c of PLLA in the presence of the stereocomplex, with (a) 15 °C/min cooling rate.



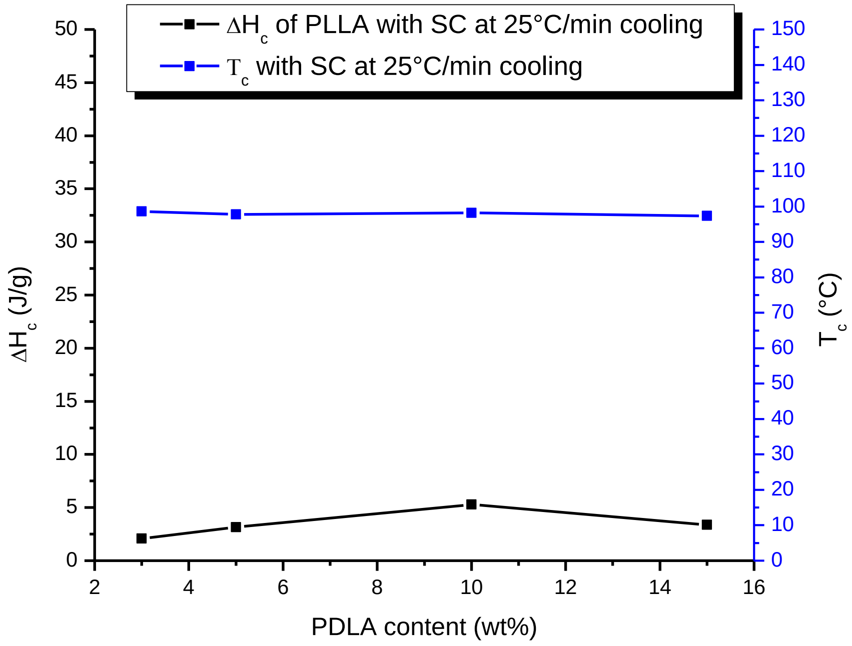
(b)

Fig. 2.13 DSC thermogram of T_c of PLLA in the presence of the stereocomplex, with (b) 25 °C/min cooling rate.



(a)

Fig. 2.14 Plots of PDLA content as a function of PLLA crystallization exotherms and T_c, upon (a) 15 °C/min cooling.



(b)

Fig. 2.14 Plots of PDLA contents versus PLLA crystallization exotherms and T_c, upon (b) 25 °C/min cooling.

In Fig. 2.13(a), the curves from top to bottom are corresponding to samples with 0-15 wt% PDLA. Crystallization peaks obtained under 15 °C/min cooling from 1-15 wt% PDLA blends are found to be around 100 °C, with much smaller crystallization exotherms. On the other hand, the crystallization exotherms in pure PLLA sample and samples containing 0.3 and 0.5 wt% PDLA are absent. In the case of non-isothermal crystallization under 25 °C/min cooling rate (Fig. 2.13 (b)), the crystallization peak in 1wt% PDLA sample has disappeared, while the crystallization extent in the rest of PDLA blends (3, 5, 10 and 15 wt%) has drastically reduced to around 5 J/g. In other word, only less than 10% of PLLA crystallized during fast cooling process..

Comparing Fig. 2.14 to Fig. 2.12, when 15 °C/min cooling rate was applied, the crystallization enthalpies become half of the amount obtained under 5 °C/min cooling, which is even smaller in case of crystallization under 25 °C/min cooling. Similarly, T_c measured from samples containing 1-15 wt% PDLA decreases around 20 °C. Eventually T_c became undetectable in sample with 1wt% PDLA, when 25 °C/min cooling was applied. The acute decrease on crystallization enthalpies and T_c could be explained as by following: When higher cooling rate is utilized, the time available for PLLA polymer chains to align and fold will be shorter, since the temperature range for one polymer to crystallize is fixed, which is between temperature under T_m and above T_g. Given that chain folding and moving to crystallization sites is a time-consuming process, when high cooling rate is applied, polymer chains will reach “frozen-state” before moving to the crystallization sites. Thus the crystallization extent was low and the enthalpies detected were much smaller when higher cooling rate was applied. Yet, comparing to the samples containing 0-1 wt% PDLA samples, the increase of PDLA still enhances PLLA crystallization.

So far, in this work, the non-isothermal PLLA crystallization process with the incorporation of PDLA has being examined. Generally, the results suggest that samples containing PDLA could give better performance during controlled crystallization (in the presence of PDLA). When the content of PDLA reached above 3 wt%, the enhancing effect became maximized, in terms of elevating crystallization enthalpy and crystallization temperature.

2.4.2 DSC Isothermal Crystallization Analysis

The purpose of this study is to understand the kinetics of crystallization at a given crystallization temperature, as well as to quantitatively compare the enhancing effect brought by different PDLA content.

a. Isothermal crystallization at given T_c quenched from 230 °C (isothermal crystallization of blends without the presence of stereocomplex)

To achieve the isothermal analysis without the presence of stereocomplex, PLLA/PDLA blends containing 0.3-15 wt% PDLA were rapidly heated (100 °C/min) to 230 °C and held for 3 min to completely melt the blends and to erase the thermal history. Samples were then quenched from 230 °C to 120 °C, and held for 20 min to detect isothermal crystallization.

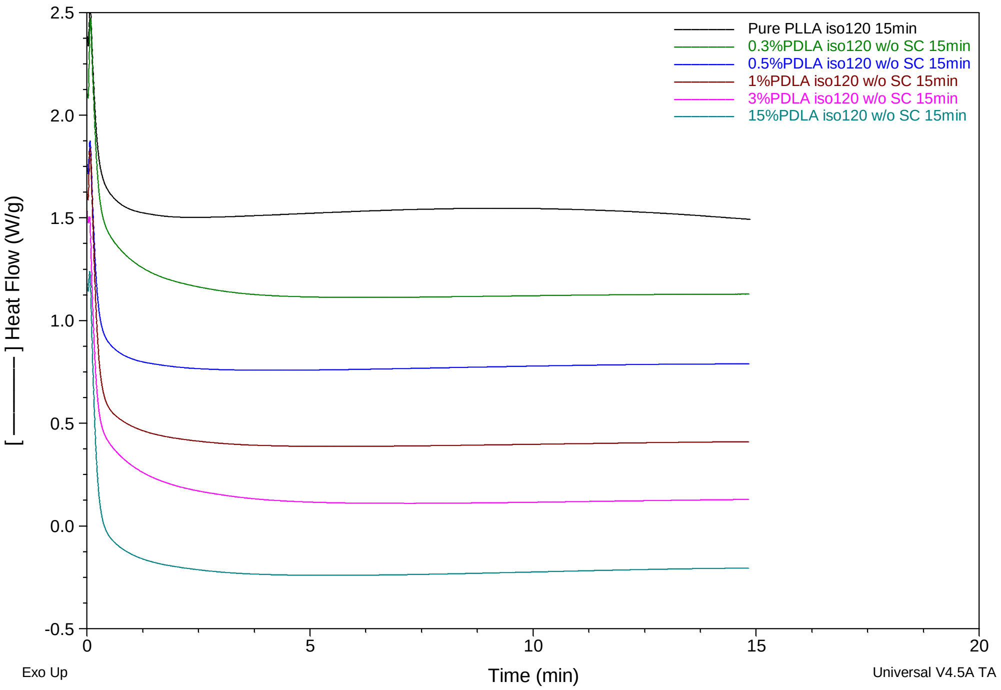


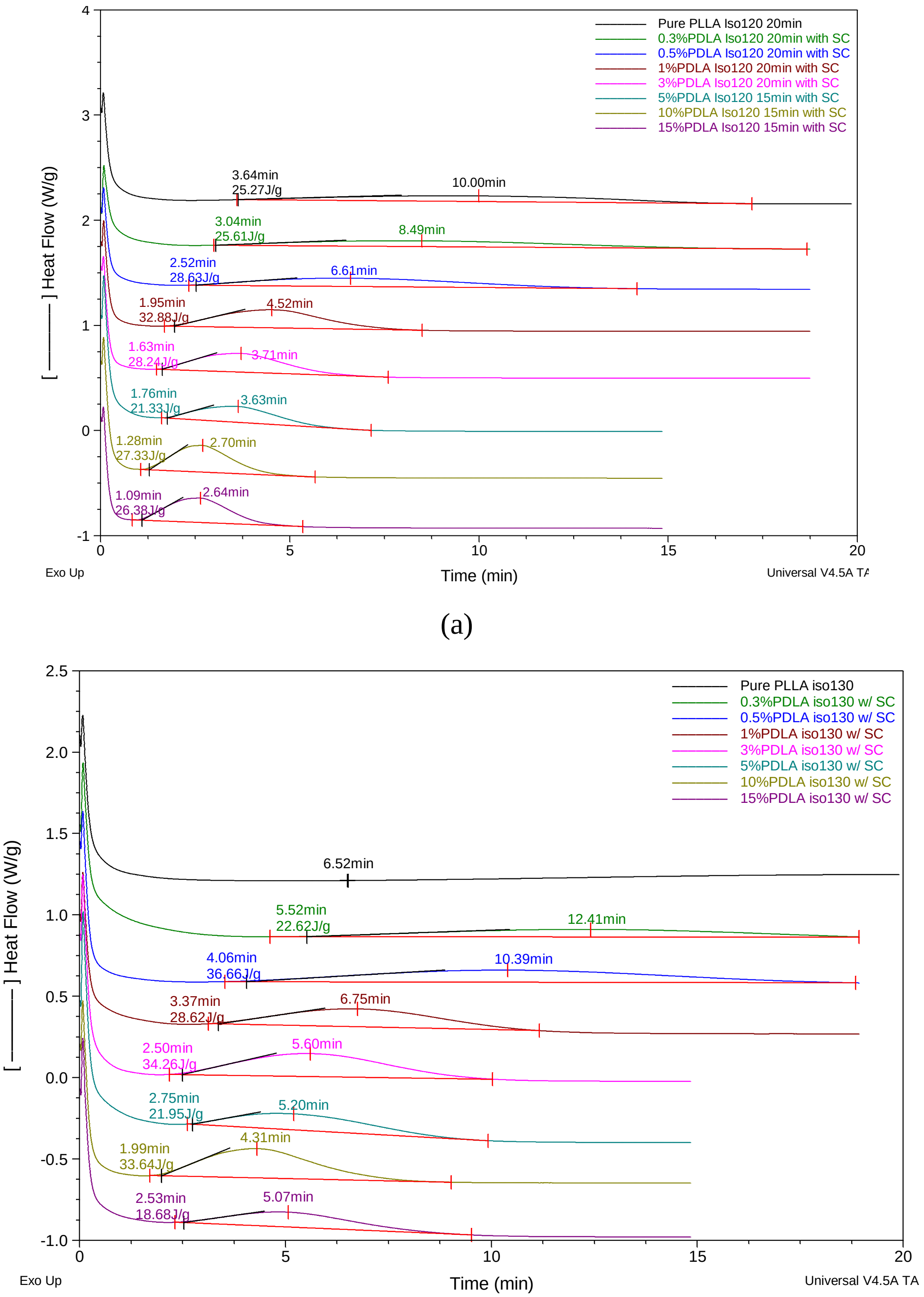
Fig. 2.15 DSC isothermal curves of samples containing 0, 0.3, 0.5, 1, 3 and 15 wt% PDLA, without the presence of SC

Fig. 2.15 shows the isothermal crystallization curves obtained from samples blended with different amount of PDLA. For all the tested samples, there is hardly or no indication of PLLA crystallization. In the case of pure PLLA sample, during non-isothermal crystallization analysis, favorable T_c has been found to be around 105 °C, and onset temperature found to be 113 °C. Thus with 15 °C difference from its crystallization temperature, the energy state seems too high for polymer chain to stabilize, then flatten and fold. Meanwhile, the supercooling is not large enough for PLLA nucleation and crystallization to take place.

In the cases of samples blended with PDLA, the absence of crystallization peak indicates that quenching from the melt without stereocomplex, the isothermal behavior of blends is almost identical with that of pure PLLA. Due to the unfavorable T_c, it is hard for PLLA crystallization to occur. Thus, the isothermal crystallization experiments in the presence of stereocomplex are conducted under different T_c, to explore the enhancing effect on PLLA crystallization brought by stereocomplex.

b. Isothermal crystallization at given T_c quenched from 190 °C (isothermal crystallization of blends in the presence of stereocomplex)

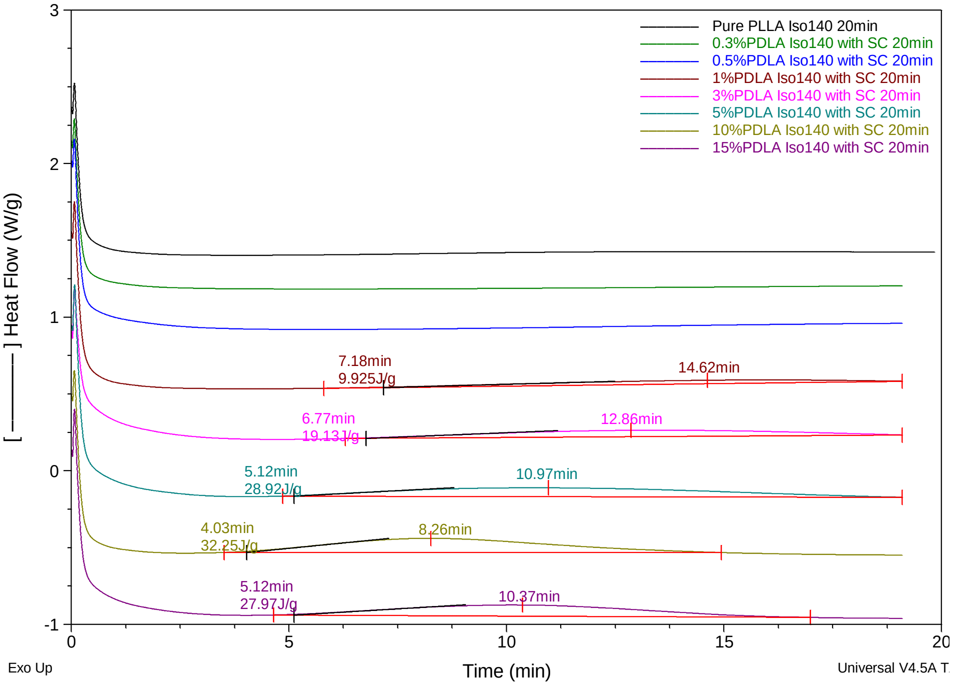
To perform the isothermal crystallization in the presence of the stereocomplex, PLLA/PDLA blends containing 0.3-15 wt% PDLA were rapidly heated (100 °C/min) to 230 °C and held for 3 min to completely melt the blends and to erase the thermal history. Then samples were quenched from 230 °C to 160 °C, and then cooled (5 °C/min) to 80 °C, allowing both stereocomplex and homopolymer to crystallize. Next, the blends were heated to 190 °C at 100 °C/min and held for 3 min, to melt the PLLA but leave SC intact. After that, the samples were quenched (100 °C/min) from 190 °C to 120, 130 and 140 °C, respectively, to be held for 15 min to conduct isothermal crystallization experiment.



(a)

(b)

Fig. 2.16 DSC data from isothermal crystallization of blends containing stereocomplex at (a) 120 °C and (b) 130 °C for 15 or 20 min.



(c)

Fig. 2.16 DSC data from isothermal crystallization of blends containing stereocomplex at (c) 140 °C, for 20 min.

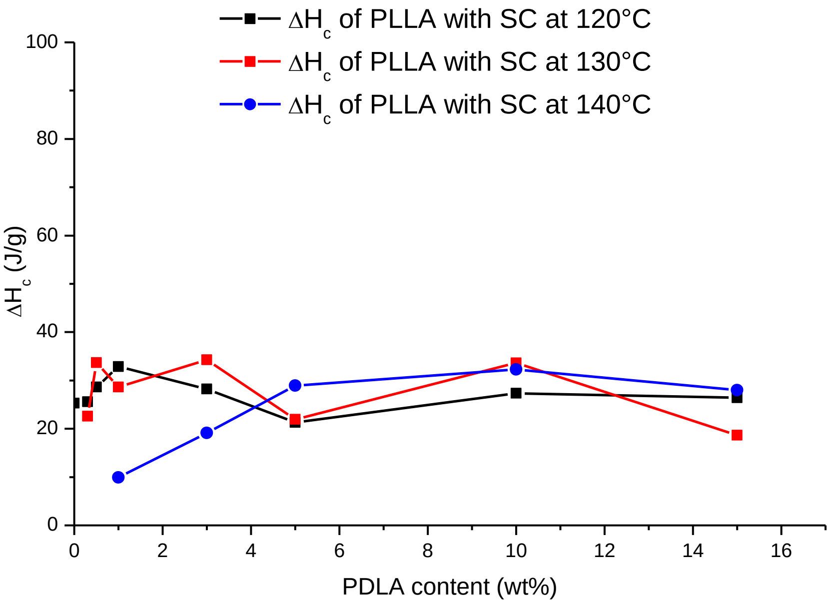


Fig. 2.17 Crystallization enthalpy of different blends with varying PDLA content obtained from isothermal crystallization at 120, 130 and 140 °C.

From Fig. 2.16, it can be concluded that at each isothermal crystallization temperature, with PDLA added, crystallization occurs faster, when compared to that of pure PLLA. The higher the T_c the samples are held to, the slower the crystallization occurs. The overall changes of crystallization enthalpy during isothermal crystallization at different temperature are shown in Fig. 2.17. It demonstrates that even though the crystallization enthalpies are distinct in different samples, only small difference observed in all samples at 120 and 130 °C, suggesting the overall extents of crystallization of samples with different amounts of PDLA was essentially the same. At 140 °C, the crystallization exotherms are undetectable in pure PLLA sample and samples containing 0.3 and 0.5 wt% PDLA. This indicates that the shortage of stereocomplex does not interact with PLLA to let the epitaxial crystallization occur under more critical conditions. This general change is mainly due to the narrowing down of the supercooling. Reduced supercooling results in reduced driving force of crystallization, hence polymer chains could not overcome the energy barrier to stabilize and to form aligned structure. Consequently, this delays or restricts crystallization. This can be seen in Fig. 2.18, providing the comparison of crystallization induction time (onset) measured in blends under different isothermal temperatures. The crystallization induction time indicates the time required for crystallization process to begin.

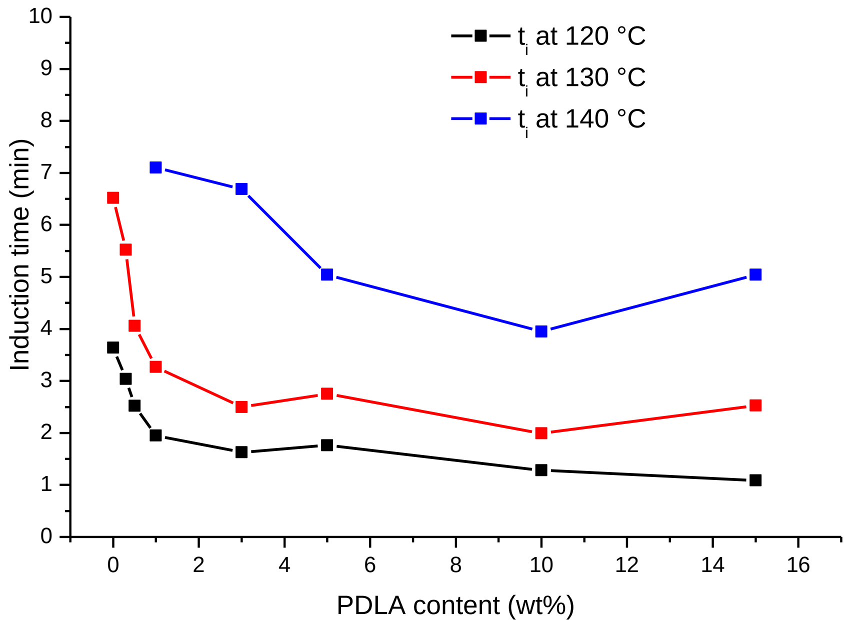


Fig. 2.18 Comparison of crystallization induction time (onset) measured in different blends of varying PDLA content under different isothermal temperature.

By plotting the crystallization induction time (onset) obtained for different blends under different isothermal temperatures, the accelerating effect brought by the stereocomplex can be illustrated clearly. Compared to the pure PLLA sample, the induction times obtained from blends containing PDLA are found to be shorter. In the 0.3-3 wt% PDLA samples, t_i decreases with the amount of PDLA, then the expediting effect becomes less obvious after 3 wt% PDLA incorporated. Again, the plateau indicates the saturated amount of SC has been formed, which brings the maximum nucleating effect on the PLLA crystallization.

The increase of t_i with increasing T_c has been reported by Tsuji et al. before, yet the expediting effect on PLLA crystallization at a given T_c showed no explicit dependence on PDLA content. [47]

To quantitatively illustrate the accelerating effect brought by the incorporation of PDLA, the crystallization half-time ($t_{1/2}$) was calculated. Crystallization half-time, is the time required for a sample to achieve half of the crystallization that it would eventually achieve. [31] By integrating the crystallization exotherms obtained from isothermal DSC curve, a relative degree of crystallinity can be calculated at any given time based on the entire area of the crystallization exotherm. A representative example from 10 wt% PDLA sample held at 120 °C for 15 min is given in Fig. 2.19. By drawing vertical and horizontal drop line, $t_{1/2}$ can be estimated to have the value of 1.5 min, for PLLA crystallization with 10 wt% PDLA at120 °C.

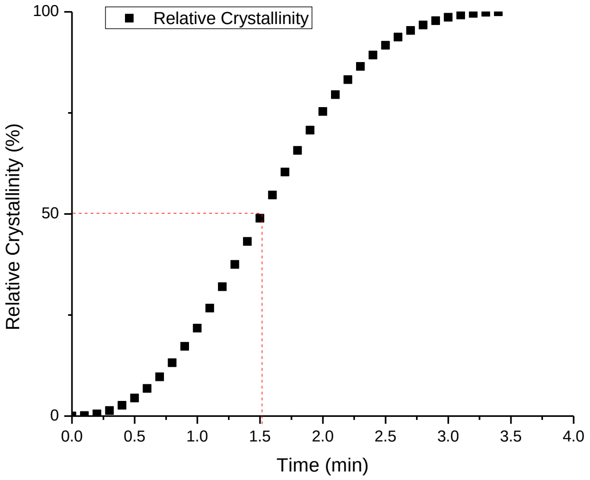


Fig. 2.19 Representative example curve for determining the isothermal crystallization half-time taken from 10 wt% PDLA sample held at 120 °C for 15 min.

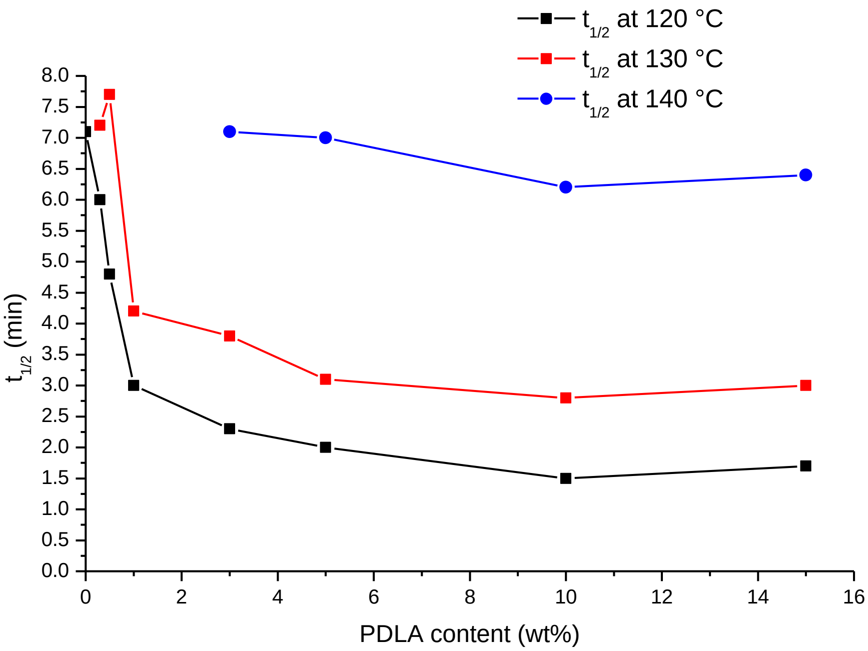


Fig. 2.20 Comparison of crystallization half-time acquired from PLLA/PDLA blends of varying compositions under different isothermal temperature.

Table 2.3 Crystallization half-time of PLLA/PDLA blends under different isothermal temperature

PDLA Content (wt %)	$t_{1/2}$ at 120°C (min)	$t_{1/2}$ at 130°C (min)	$t_{1/2}$ at 140°C (min)
0	7.1	N/A	N/A
0.3	6	7.2	N/A
0.5	4.8	7.7	N/A
1	3	4.2	N/A
3	2.3	3.8	7.1
5	2	3.1	7
10	1.5	2.8	6.2
15	1.7	3	6.4

The crystallization half-times were plotted and listed in Fig. 2.20 and Table 2.3, respectively. As shown in Fig. 2.20, the tendency of the change on $t_{1/2}$ versus the change on PDLA content under different temperatures is clearly illustrated: at each temperature, the $t_{1/2}$ is notably shortened with the amount of PDLA added. Yet, this tendency becomes less obvious in samples with PDLA content above 3 wt%, regardless of isothermal temperature. The smallest $t_{1/2}$ values at each isothermal temperature can be found from the sample with 10 wt% PDLA, as 1.5 min at 120 °C, 2.8 min at 130 °C and 6.2 min at 140 °C. The $t_{1/2}$ values obtained from sample containing 3 wt% PDLA, however, are always close the values obtained from sample with 10 wt% PDLA. At 130 and 140 °C, the $t_{1/2}$ values are not applicable in pure PLLA and samples containing low PDLA content, suggesting continuous enhancing effect on PLLA crystallization could only be provided, if more than 3 wt% PDLA is blended with PLLA. This nucleating effect was found by Schmidt et al. and Anderson et al. Schmidt et al. found the smallest $t_{1/2}$ at 140 °C was 75 sec from sample blended with 10 wt% PDLA (M_w around 100,000 g/mol) prepared by solution precipitation method, while Anderson et al. reported a $t_{1/2}$ smaller than 1 min at 140 °C from sample containing 3 wt% PDLA (M_w = 14,000 g/mol) prepared by hot mixing method. Moreover, obtained from sample with 6 wt% talc, the $t_{1/2}$ was less than 1 min at 120 °C, and was 6.5 min at 140 °C. [49] Here it should be noted that, talc is popular as industrially used nucleating agent. The discrepancy between the value obtained here and the one reported by Anderson et al. is presumably due to the sample preparation method. Using hot melt-mixing method, PLLA and PDLA can be mixed better, resulting in stronger interaction during crystallization.

To understand the effect of SC on crystallization kinetics the Avrami equation was used. Recalling equation (1-2), and equation (1-3), by plotting $lg[-ln(1-Xc)]$ versus lgt, n

can be obtained from the slope, and *lgk* from the intercept. Here, the X_c is the relative degree of crystallinity obtained by integrating the isothermal exotherms. Fig. 2.21 shows a representative example of the plot from pure PLLA isothermal crystallization at 120 °C.

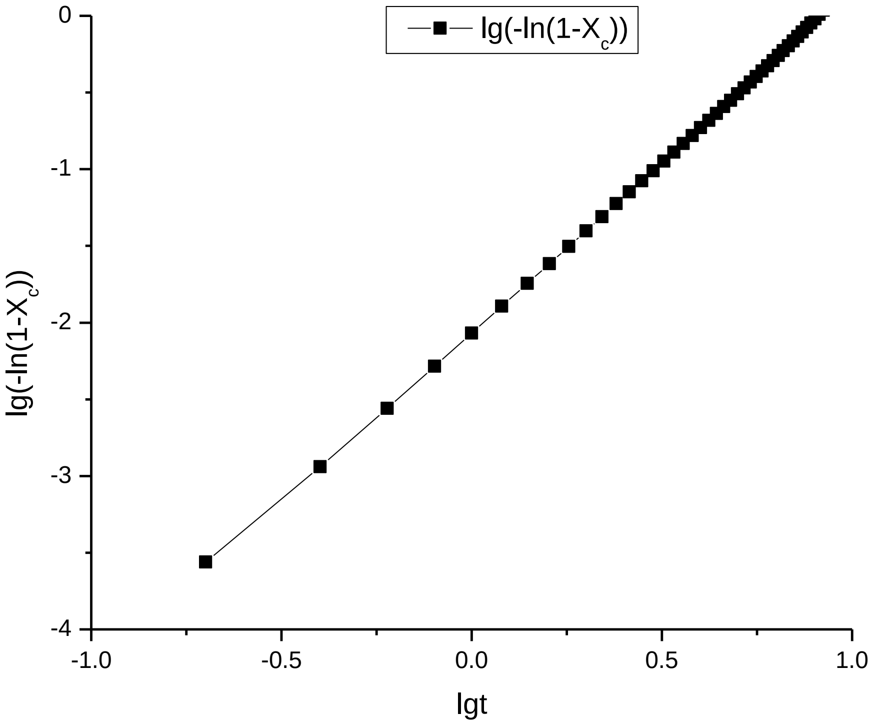


Fig. 2.21 Representative example curve for determining Avrami exponent *n* and crystallization rate constant *k* from pure PLLA sample held at 120 °C for 20 min.

In Fig. 2.21, *n* is given as the slope and *lgk* as the intercept. Given that the crystallization linear growth rate, G is proportional to $1/t_{1/2}$, then G can be calculated as a function of $t_{1/2}$, for different temperatures. [50] Obtained *n* and *k* results are given in Table 2.4.

Table 2.4 Isothermal DSC results of PLLA/PDLA blends

	At 120 °C		At 130 °C		At 140 °C	
PDLA content (wt%)	*n*	*k* (min^{-1})	*n*	*k* (min^{-1})	*n*	*k* (min^{-1})
0	2.81	0.009111	N/A	N/A	N/A	N/A
0.3	2.25	0.012302	2.22	0.008661	N/A	N/A
0.5	2.31	0.018499	2.64	0.003166	N/A	N/A
1	2.7	0.035694	2.5	0.019174	N/A	N/A
3	2.5	0.086398	2.49	0.024955	N/A	N/A
5	2.38	0.13316	2.3	0.051368	2.23	0.009042
10	2.34	0.268393	2.63	0.046217	2.41	0.008534
15	2.7	0.16543	2.26	0.05788	2.41	0.007906

The estimated *n* values are ca. 2.5, suggesting the growth of PLLA crystallites is between 2 - dimensional (disc) and 3 - dimensional (sphere), according to the theoretical value given in the text book. [24] As shown in Table 2.4, except for the *n* value of pure PLLA (2.91), other values are mostly away from the theoretical value of spherulite growth. This discrepancy could be attributed to the system error happened during extracting slopes from *lg [-ln(1-Xc)]* versus *lgt* plots. Or with these values the difference morphology of the crystallites in different samples can be expected.

With the increase of PDLA content, the crystallization rate constant *k* also increased. This result suggests the overall PLLA crystallization process could be expedited by the existence of stereocomplex.

2.4.3 Comparison of the Effectiveness of the Varying Amount of the Stereocomplex as Nucleating Agent, by Using a Nucleation Efficiency Scale

To quantitatively evaluate the effectiveness of nucleating agents, the self-nucleation process is used as reference, because of the strong and ideal nucleating effect, which has been found to have in this process. [51] This nucleation is due to the residual nuclei that are strong enough to survive the initial melt conditions. Self-nucleation is considered to be the strongest and ideal because the crystallites are well dispersed during the initial melting process, and the interaction between polymer melt and nucleating surface are highly favorable because of the identical chemical constituency and crystal lattice. [52] The highest efficiency occurs with the greatest self-nucleation concentration, in contrast the lowest efficiency occurs in the absence of nucleation sites. The latter case refers to the crystallization from pure polymer melt.

Thus, in comparison with the crystallization temperature obtained in self-nucleation process, the enhancing effect brought by hetero nucleating agents can be actually measured, with the established nucleating efficiency model given by Fillon et al. and illustrated by Schmidt et al. in terms of PLLA. [25, 48]

Recalling equation (1-4), $NE = \left(\frac{T_c - T_c^{min}}{T_c^{max} - T_c^{min}}\right) \times 100$, to apply this given nucleation efficiency scale, it is required to determine the upper and lower limit crystallization temperature at first, which should be obtained from self-nucleation PLLA crystallization. Then with already obtained crystallization temperature (T_c) from PLLA/PDLA blends non-isothermal crystallization with 5°C/min cooling rate, the power of different content of stereocomplex can be quantified.

Here, T_c^{min} has been already determined by performing PLLA homopolymer crystallization from complete polymer melt (200 °C). After complete melting, there are no PLLA nuclei left, hence the melt crystallization would begin with no nuclei existing, suggesting that the lowest crystallization temperature T_c^{min} can be obtained. T_c^{min} has been determined earlier in this study, to be 103.36 °C.

Next step is to acquire the $\mathrm{T_c^{max}}$, which i the highest crystallization temperature obtained during self-nucleation crystallization, meaning to crystallize with the nuclei residue. To obtain the T_c^{max}, Fillon et al. and Schmidt and Hillmyer have already illustrated a feasible way in early study. [25, 48] The trickiest part is to keep the self-nuclei residue during melting. Thus, the final heating temperature should be controlled. Fortunately, this partial melting of self-nuclei can be achieved by holding the polymer at temperature slightly above T_m, within its melting zone. Since polymer still stays within its melting zone, so that part of strong crystallites will not be melted. These crystallites will then become the nuclei in the next crystallization step, to initiate self-nucleation crystallization. If maximum amount of strong crystallites can be preserved, then the highest crystallization temperature can be obtained (T_c^{max}). [25] Thus, different temperatures were selected as the final heating temperature. Fig. 2.3 has already shown the T_m (177.75 °C) of PLLA utilized in this study. Thus 178, 179 and 180 °C were selected as final heating temperature, to keep most of strong crystallites, which can elevate the crystallization temperature by self-nucleating the PLLA crystallization T_c^{max}.

To experimentally obtain this T_c^{max}, PLLA samples were rapidly heated (100 °C/min) to 200 °C and held for 3 min to completely melt polymer and to erase the thermal history. Then samples were quenched from 200 °C to 160 °C, then cooled (5 °C/min) to 80 °C, allowing PLLA homopolymer to crystallize. Next, the samples were rapidly heated (100 °C/min) up to selected temperatures (178, 179 and 180 °C) within PLLA melting zone, one temperature a time. After that, the samples were cooled (5 °C/min) from 190 to 60 °C to obtain the crystallization temperature with nuclei preserved in previous step. Different crystallization temperatures obtained are shown in Fig. 2.22.

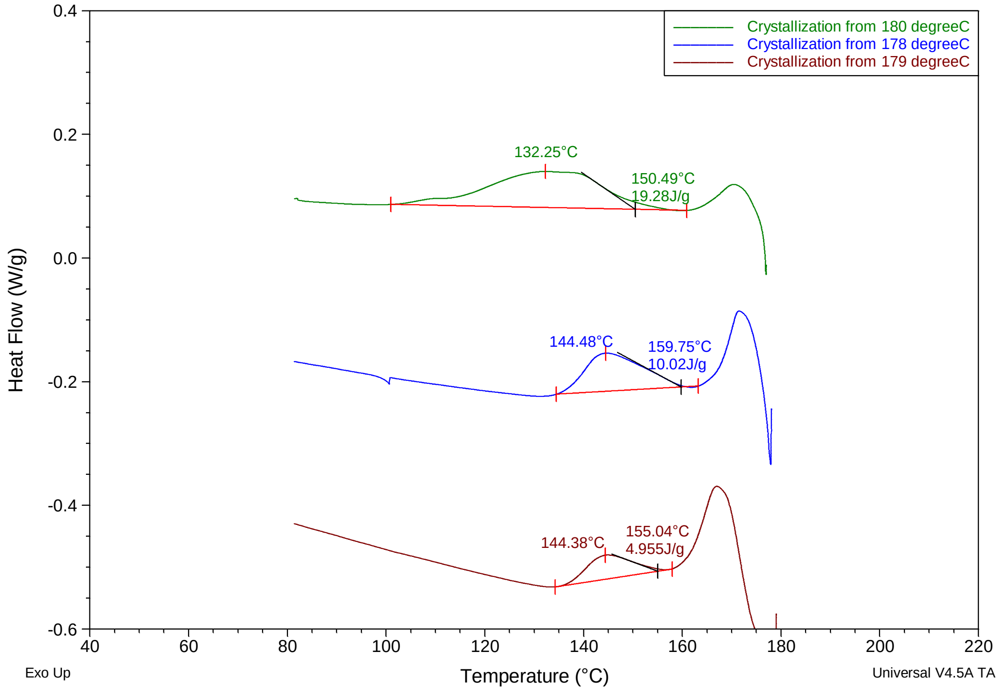


Fig. 2.22 Determination of T_c^{max}.

From the plot, T_c^{max}, the highest crystallization temperature found to be 144.5 °C, from the sample held at 178 °C then crystallize at 5 °C/min. This value was reported to be at 142.9 °C by Anderson et al. and 157 °C by Schmidt et al. [25, 43] The 13 °C difference may be due to the lower M_w of PLLA utilized by Schmidt et al. could have better mobility when crystallizing. The general improvement of the crystallization temperature supports the self-nucleation theory and shows the remarkable nucleating effect brought by strong nuclei residue preserved during partial melting.

Thus far, the lower limit crystallization temperature of nucleation efficiency scale, T_c^{min}, and the upper limit $\mathrm{T_c^{max}}$ have been successfully found. Now with the $\mathrm{T_c^{max}}$, T_c^{min} and T_c obtained from samples containing various PDLA content, the nucleation efficiency values were calculated and shown in Table 2.5.

Table 2.5 Nucleation efficiency data from samples containing different amount of PDLA

PDLA content (wt%)	$\mathrm{T_c}$ (°C)	Nucleation efficiency (%)
0	103.36	0
0.3	102.50	-2
0.5	104.22	2
1	107.90	11
3	118.84	38
5	121.16	43
10	124.31	51
15	121.19	43

As shown in Table 2.5, within samples containing 0.3-15 wt% PDLA, the highest nucleation efficiency with the value of 51% is found in sample with 10 wt% PDLA. The minus sign on the nucleation efficiency for the sample containing 0.3 wt% PDLA, suggests that the crystallization temperature is lower than the lower limit $\mathrm{T_c}$ of pure PLLA. A significant increase of the nucleation efficiency value is found starting from sample with 3 wt% PDLA, suggesting PLLA crystallization could be greatly enhanced. Yet, the nucleation efficiency values are leveling off from sample with 3 wt% PDLA, indicating the maximum enhancement brought by stereocomplex has reached. Comparing with the nucleation efficiency values obtained by Anderson et al. and Schmidt et al., the values found here are much lower, while they had several groups giving nucleation efficiency value around 100%. [25, 43] The discrepancy may be ascribed as different molecular weight PLLA applied (lower than 100,000 g/mol in both their studies, compared to the 340,000 g/mol PLLA used here) and different sample preparation method adopted (hot melt-mixing was adopted by Anderson et al. while solvent casting was performed in this work). Larger M_w may reduce the mobility and increase the viscosity, so that the transferring of chain segments to crystallization sites may become more difficult, compare to small M_w polymer crystallization.

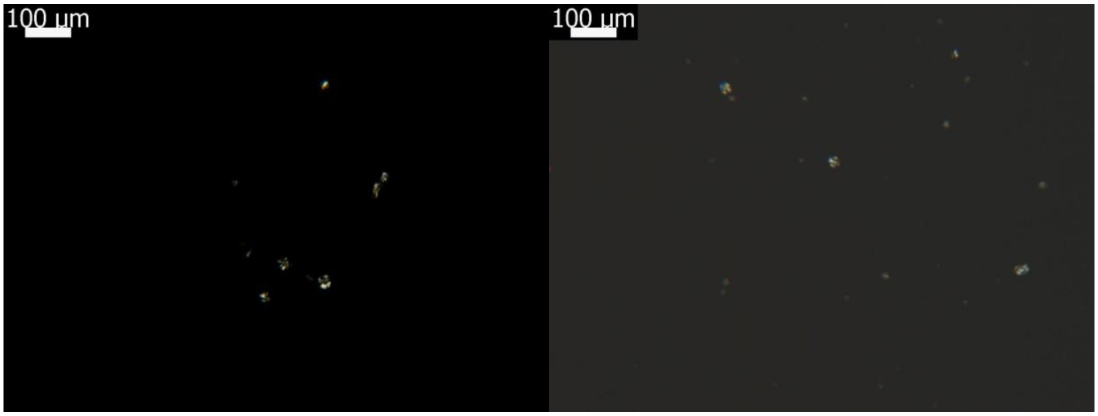
2.4.4 PLLA/PDLA Crystallization Studied by Hot Stage Polarized Optical Microscopy

The purpose of using hot stage polarized optical microscope (HSPOM) was to visually confirm the thermal behaviors and thermal properties found with the DSC However, attempts to calculate the crystallization growth rate were not successful , because of the small-sized crystallites and the limitation brought by the low magnification of microscope. The magnification in hot stage polarized optical microscope study was 6.3 times.

2.4.4.1 Observation of Non-isothermal Crystallization Behavior

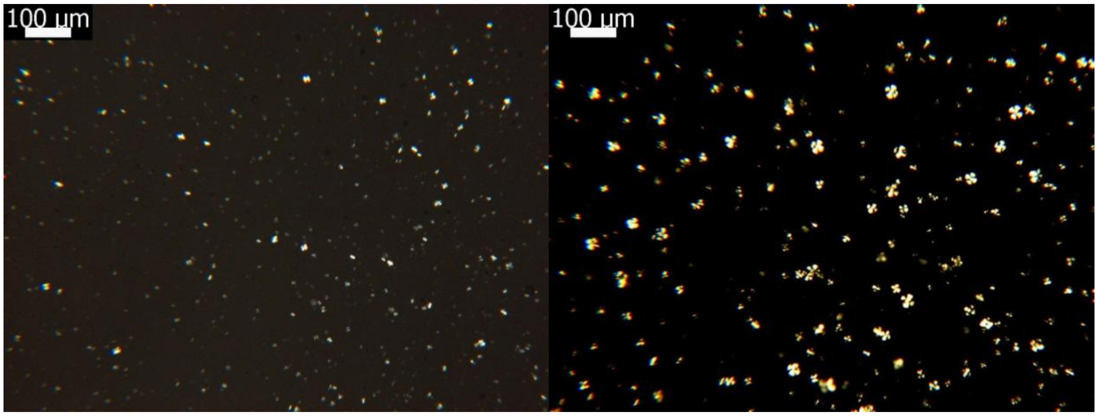
To visually observe the non-isothermal crystallization and melting behavior, samples containing 0-15 wt% PDLA were heated (20 °C/min) to 230 °C and held for 3 min to completely melt and erase the thermal history. Then samples were cooled (20 °C/min) from 230 °C to 160 °C, then cooled (5 °C/min) to 80 °C, to observe the non-isothermal crystallization behavior. The blends were then heated to 230 °C at 10 °C/min and held for 3min, to observe the melting behavior.

During cooling from 160 °C to 80 °C, a few tiny specks (i.e. nuclei) appeared in samples containing 0, 0.3, 0.5 and 1 w% PDLA at ca. 120-125 °C. In the case of samples containing 3, 5, 10, 15 wt% PDLA, more specks appeared at higher temperature, ca. 130-145 °C, with the increase of PDLA content. The increasing temperature at which the first crystallite/ nucleus appeared can be related with the increasing onset temperature obtained from DSC analysis earlier in this study. Fig. 2.23 shows the HSPOM photomicrographs of PLLA containing 0-15 wt% PDLA at 120 °C, during non-isothermal crystallization from 160 °C, at 5 °C/min.

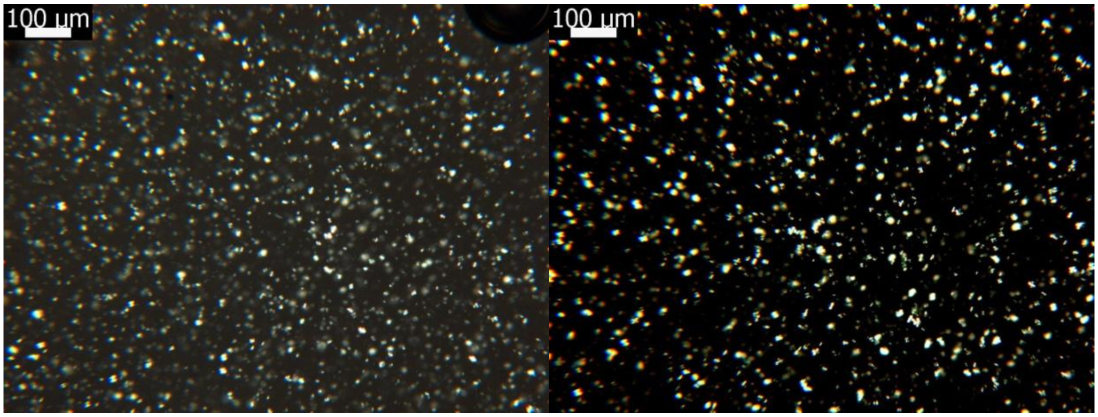


(0 wt% PDLA) (0.3 wt% PDLA)

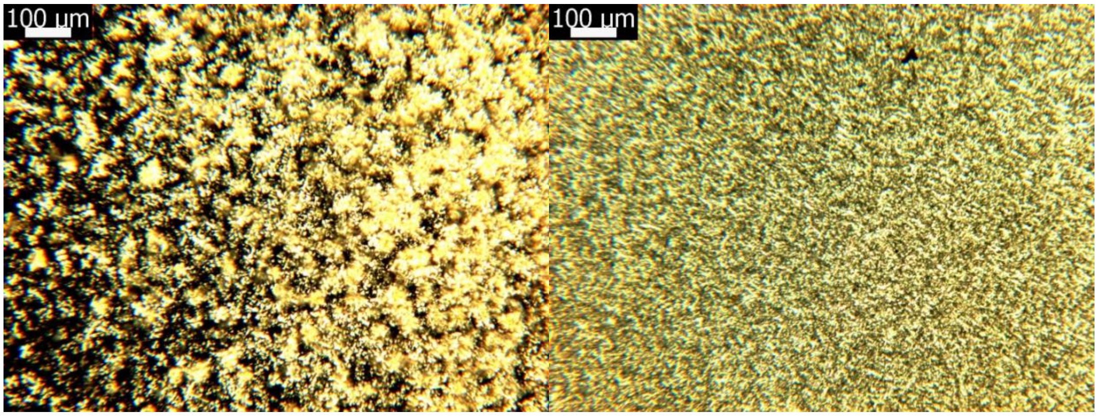
Fig. 2.23 HSPOM photomicrographs of PLLA containing 0, 0.3, 0.5, 1, 3, 5, 10, 15 wt% PDLA at 120 °C, during non-isothermal crystallization from 160 °C, at 5 °C/min.



(0.5 wt% PDLA) (1 wt% PDLA)



(3 wt% PDLA) (5 wt% PDLA)

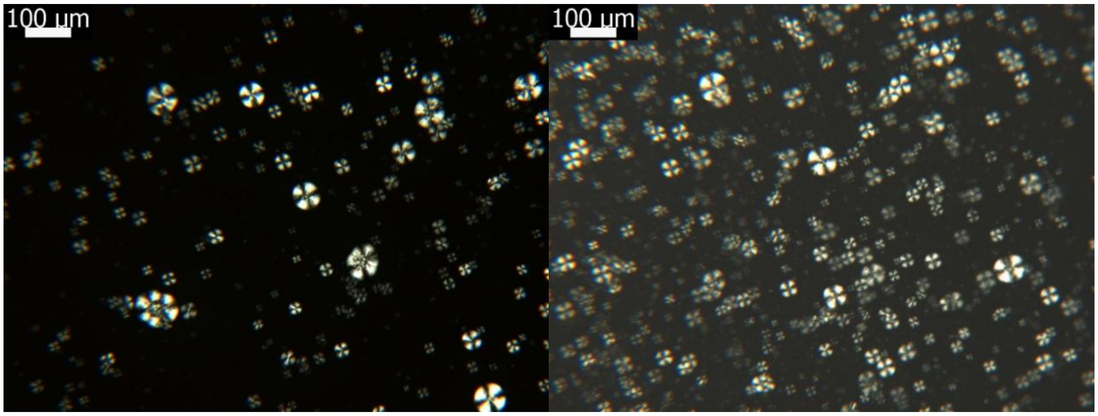


(10 wt% PDLA) (15 wt% PDLA)

Fig. 2.23 (Continued) HSPOM photomicrographs of PLLA containing 0, 0.3, 0.5, 1, 3, 5, 10, 15 wt% PDLA at 120 °C, during non-isothermal crystallization from 160 °C, at 5 °C/min.

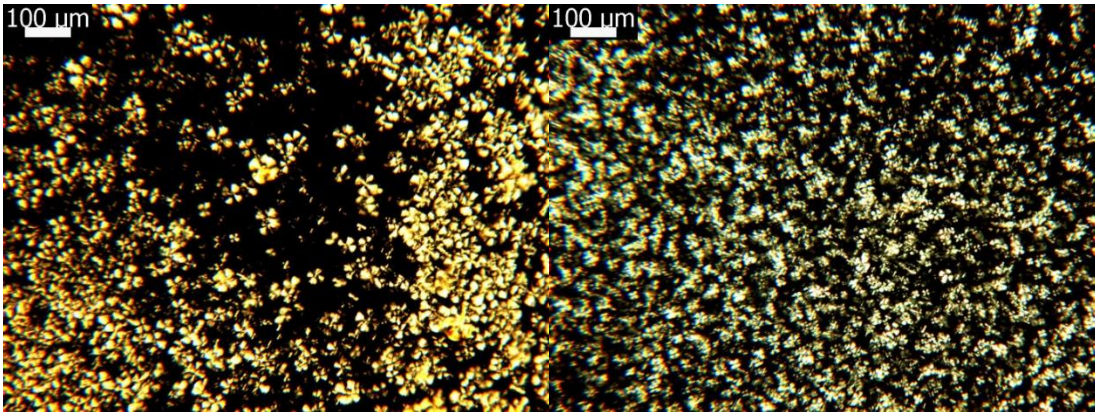
With the crystallization progressing, the spherulite size kept increasing, and new crystallization sites were created. During the crystallization process of pure PLLA sample at 110-100 °C, acceleration on crystallite growth was observed, indicating the T_c range (Fig. 2.1). The same phenomenon happened between 120-100 °C in blends, suggesting the T_c shifts because of the nucleating effect brought by stereocomplex. It has to be stressed here, due to the limited heating/cooling rate (maximum 20 °C/min) and fan cooling system on hot stage, the quenching step applied during DSC analysis was not possible to perform here. Thus, the lower cooling rate may induce the early crystallization of SC, which provides the nucleating effect, during the 1st cooling.

When the temperature was below 100 °C, the overall growth rate was found to be much lower, indicating that the mobility of polymer chain segments decreased. Fig. 2.24 shows the photomicrographs of all the samples at 80 °C.

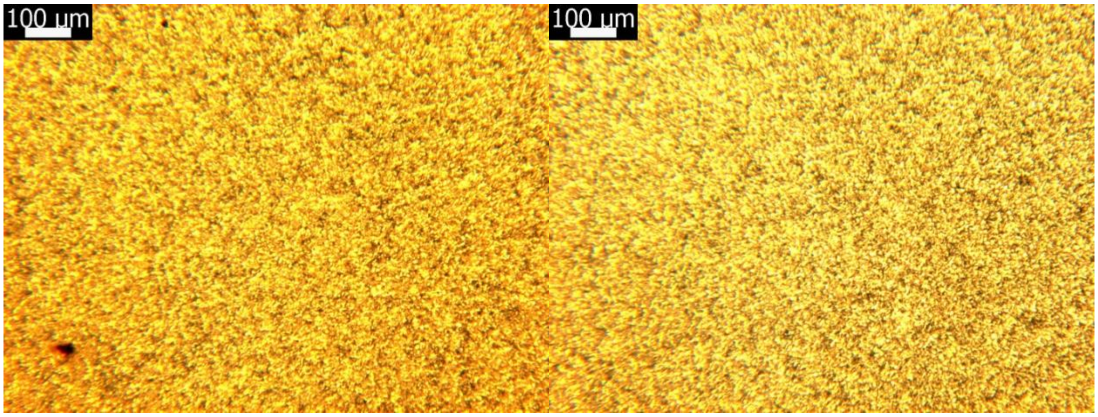


(0 wt% PDLA) (0.3 wt% PDLA)

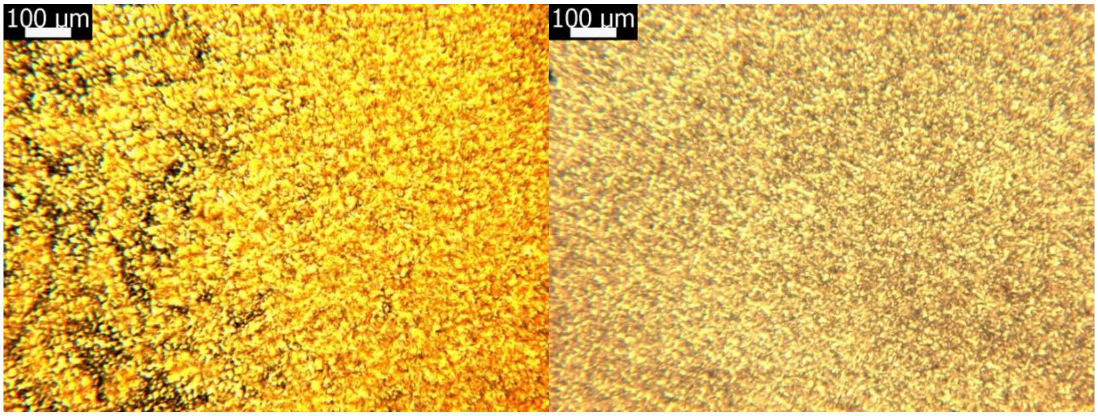
Fig. 2.24 Photomicrographs of PLLA containing different PDLA content at 80 °C after crystallizing from 160 °C at 5 °C/min.



(0.5 wt% PDLA) (1 wt% PDLA)



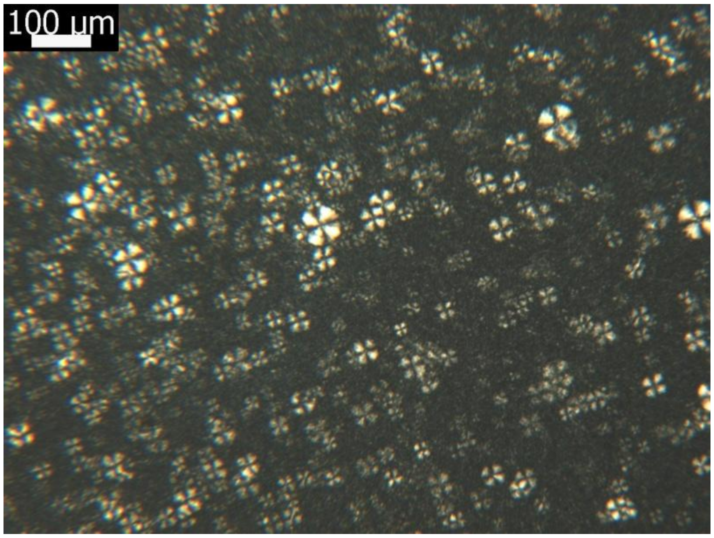
(3 wt% PDLA) (5 wt% PDLA)



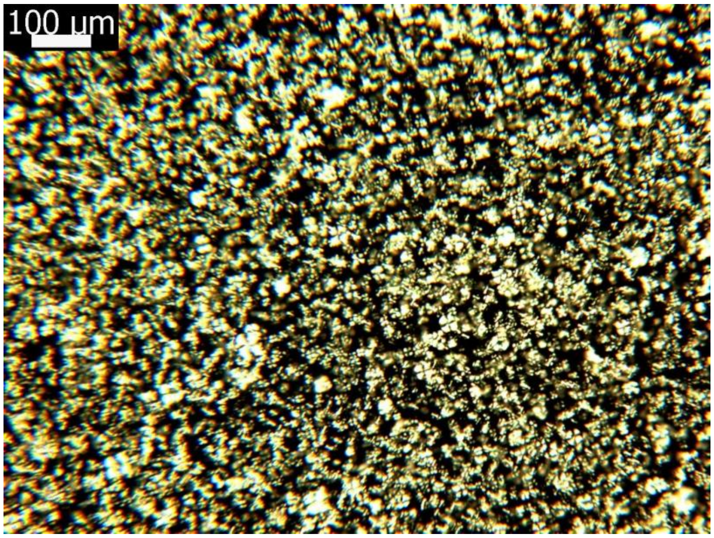
(10 wt% PDLA) (15 wt% PDLA)

Fig. 2.24 (Continued) Photomicrographs of PLLA containing different PDLA content at 80 °C after crystallizing from 160 °C at 5 °C/min.

Upon heating from 80 - 230 °C at 10 °C/min, the recrystallization was found between 100-130 °C in samples containing 0.3-1 wt% PDLA (given in Fig. 2.25), and was in good agreement with the DSC curves obtained earlier.(Fig. 2.3)

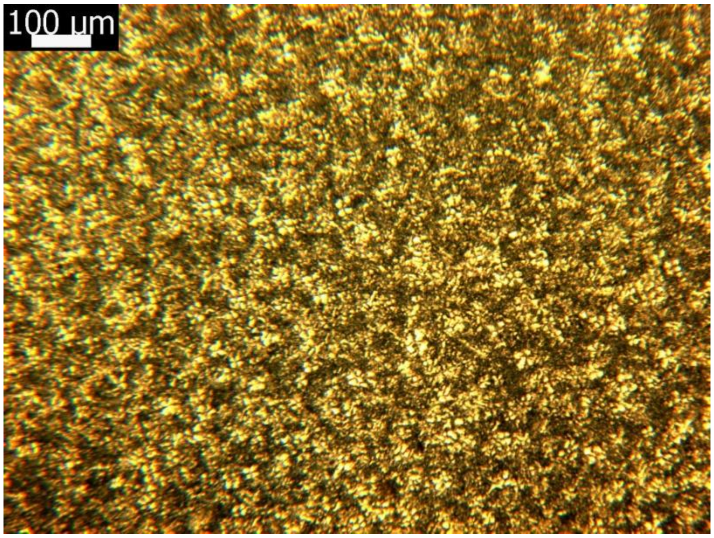


(a) 0.3 wt% PDLA



(b) 0.5 wt% PDLA

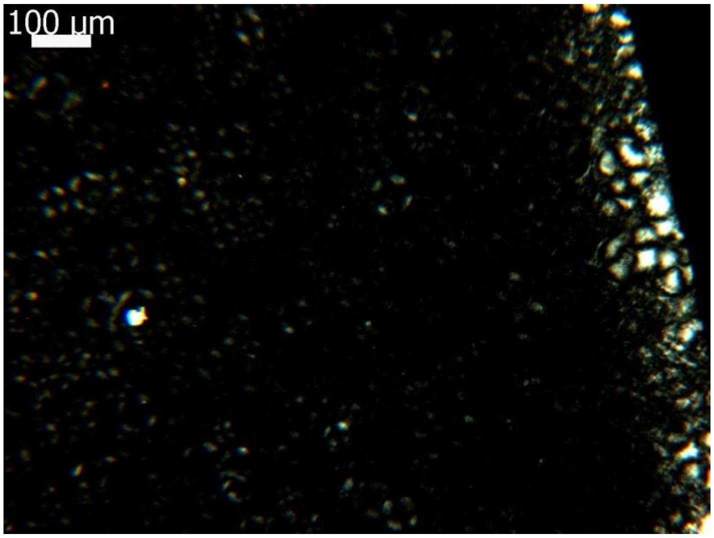
Fig. 2.25 Photomicrograph of recrystallization observed from PLLA blended with (a) 0.3 wt% PDLA and (b) 0.5 wt% PDLA.



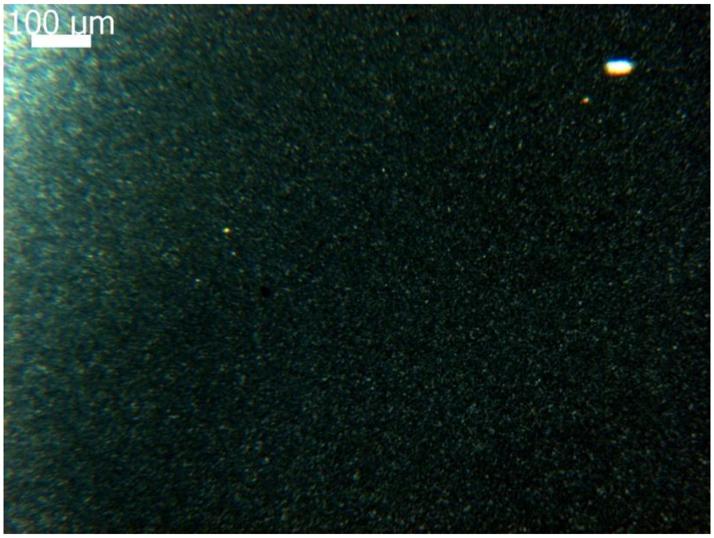
(c) 1 wt% PDLA

Fig. 2.25 Photomicrograph of recrystallization observed from PLLA blended with (c) 1 wt% PDLA.

In all the samples, the melting of PLLA crystallites started at temperature slightly above 170 °C, and completely or mostly disappeared around 185 °C, indicating the melting range of PLLA crystallites (Fig. 2.3 and Fig. 2.7). Here, from the DSC melting curve, it has been shown that the stereocomplex will still exist above the melting range of pure PLLA, and it will begin melting again at around 210 °C (Fig. 2.7). However, the corresponding phenomenon was only observed within samples containing 10 and 15 wt% PDLA. After heated above 190 °C, few spherulites in 10 wt% PDLA sample and few specks in 15 wt% PDLA sample still existed. This phenomenon is shown in Fig. 2.26. Heated above 215 °C, these crystallites melted again, and completely disappeared at 225-228 °C.



(a) 10wt% PDLA sample



(b) 15wt% PDLA sample

Fig. 2.26 Photomicrograph of stereocomplex observed in (a) 10 wt% PDLA sample, (b) 15 wt% PDLA sample at 200 °C.

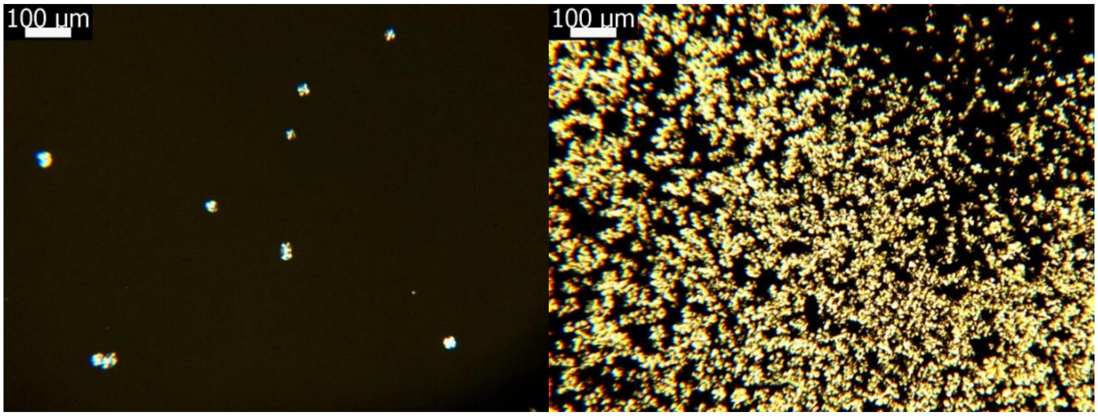
The existence of SC above 200 °C was also observed by Anderson et al., from PLLA samples containing 0.5 and 3 wt% PDLA. [43]

The absence of SC above 190 °C in sample containing low amount of PDLA may be due to the low magnification (6.3 times) limited by the microscope.

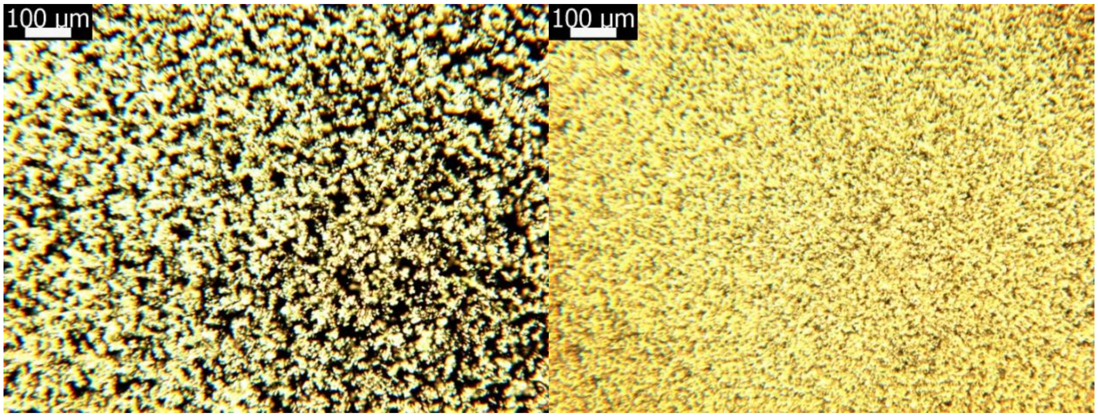
2.4.4.2 Observation of Isothermal Crystallization Behavior

To visually observe the isothermal crystallization behavior, the samples containing 0-15 wt% PDLA were heated (20 °C/min) to 230 °C and held for 3 min to completely melt and to erase the thermal history. Next, samples were cooled (20 °C/min) from 230 to 160 °C, then cooled (5 °C/min) to 80 °C, to crystallize. After that, samples were heated (20 °C/min) to 190 °C and held for 3 min to melt PLLA crystallites. Then the samples were cooled (20 °C/min) from 190 °C to 130 °C, and held 10 min, to perform the isothermal crystallization. Photomicrographs were taken every 30 sec since the beginning of isothermal crystallization, to record the crystallization growth.

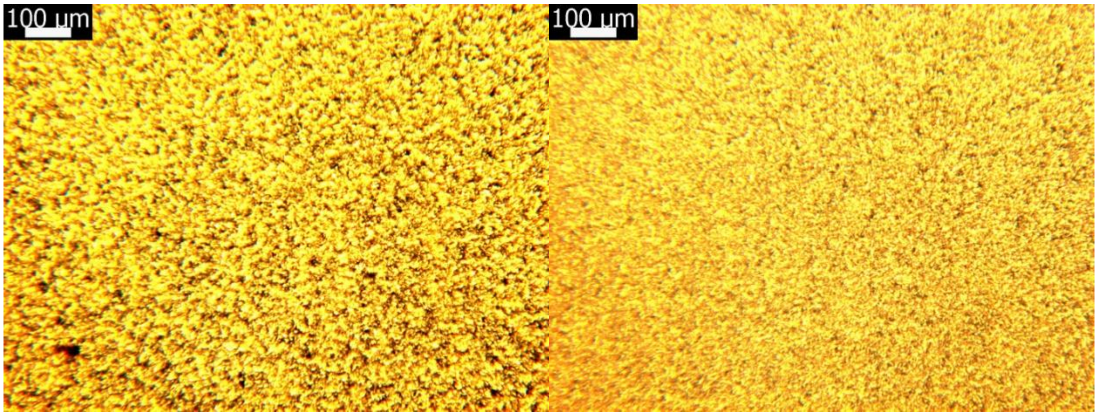
In pure PLLA sample, the 1st spherulite appeared at 1.5 min, yet the growing of s spherulite was slow. During crystallization, few new crystallization sites were created. While in samples containing PDLA, crystallites started appearing at 0.5-1 min. With the increasing of PDLA content, the increase on number of initial crystallization sites and the decrease of their size were observed through POM. During crystallization process, much more new sites were created, comparing to that of pure PLLA. Fig. 2.27 shows the photomicrographs during isothermal crystallization at 3 min.



(0 wt% PDLA) (0.3 wt% PDLA)

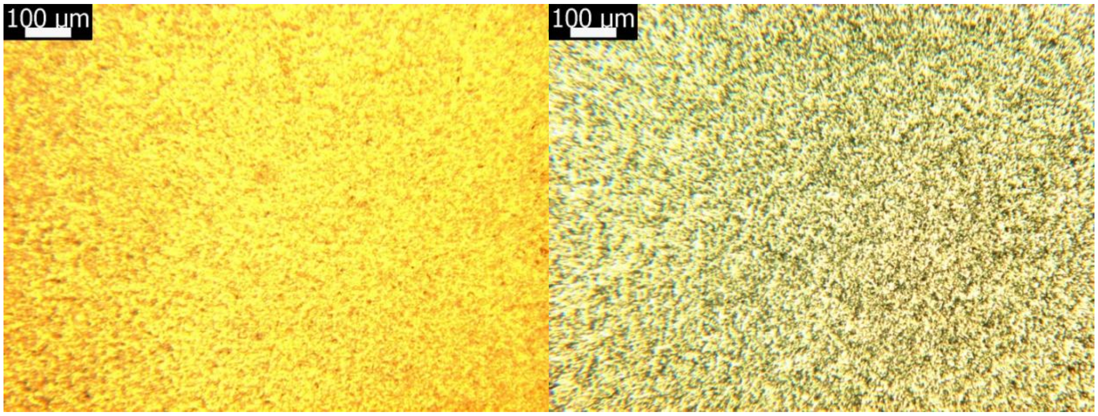


(0.5 wt% PDLA) (1 wt% PDLA)



(3 wt% PDLA) (5 wt% PDLA)

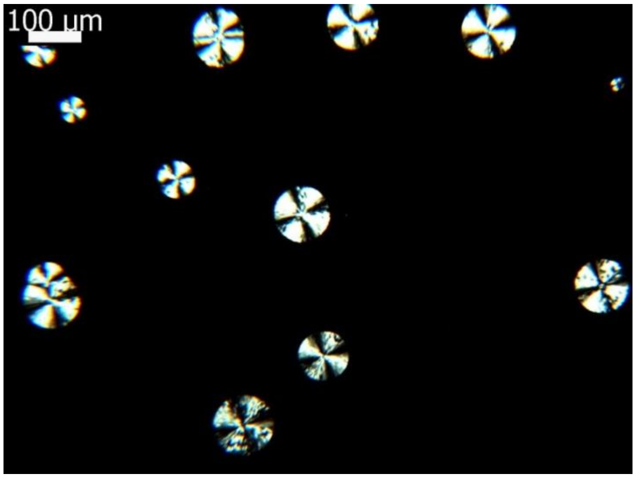
Fig. 2.27 Photomicrographs of samples during isothermal crystallization at 3 min.



(10 wt% PDLA) (15 wt% PDLA)

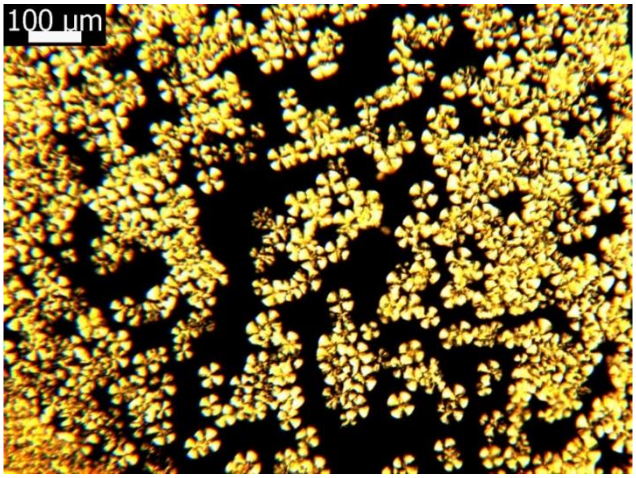
Fig. 2.27 (Continued) Photomicrographs of samples during isothermal crystallization at 3 min.

As we can see in Fig. 2.27, the morphology of 1-15 wt% PDLA is nearly identical. This again suggests the saturated nucleating effect brought with the increase of PDLA content. In contrast, in samples containing 0-0.5 wt% PDLA, the continuous spherulitic growth was observed throughout the entire isothermal crystallization experiment. Fig. 2.28 compares the photomicrographs taken from samples containing 0, 0.3 and 3 wt% PDLA, respectively, upon isothermal crystallization at 10 min.

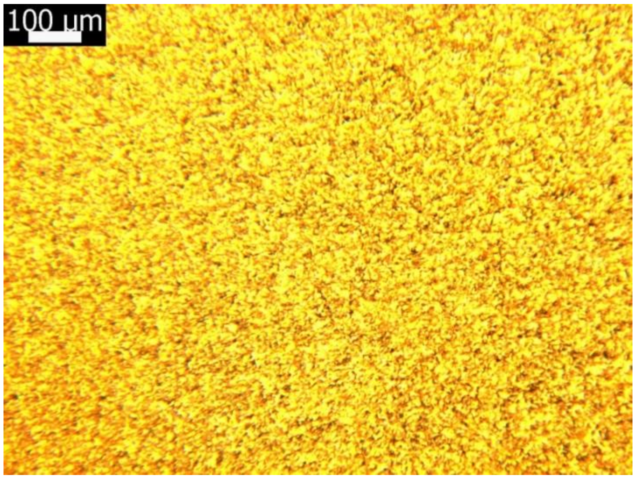


(Pure PLLA)

Fig. 2.28 Photomicrographs of samples containing 0, 0.3 and 3 wt% PDLA, upon isothermal crystallization at 10 min.



(0.3 wt% PDLA)



(3 wt% PDLA)

Fig. 2.28 (Continued) Photomicrographs of samples containing 0, 0.3 and 3 wt% PDLA, upon isothermal crystallization at 10 min.

The increase of PLLA spherulite density with PDLA content was observed by Tsuji et al. and ascribed as the nucleating effect brought by the additional PDLA. [47] Similarly, Anderson et al., Schmidt et al., Narita et al., Brucho et al. and Yamane et al. also reported the increase on spherulite density with PDLA content. [25, 43, 44, 45, 46, 53]

Additionally, the images taken from samples containing 3-15 wt% PDLA demonstrate the absence of the black cross, the indicative of spherulite structure. Instead, the images show the defective crystalline structure and the irregular orientation of the lamellas. Recalling the *n* values (Avrami exponent) given in Table 2.4, the discrepancy between the calculated values and theoretical n value for spherulite growth (*n*=3), could be related to these irregular growths. The similar morphology was observed from most non-equimolar PLLA/PDLA blends studied earlier. [25, 45, 53] Tsuji et al. showed the photomicrographs of the mixture of PLLA with 10 wt% PDLA with high magnification (Fig. 2.29 B), demonstrating the less ordered structure (regions on the top right and bottom left) than that of equimolar PLLA/PDLA mixture (Fig. 2.29 A). [53]

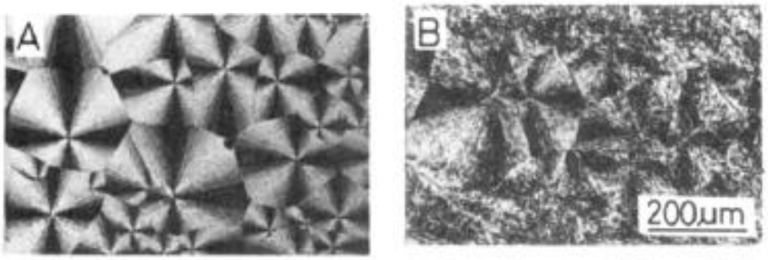


Fig. 2.29 A. Photomicrographs of equimolar mixture of PLLA/PDLA, B. Photomicrographs of mixture of PLLA with 10 wt% PDLA. [53]

As Tsuji et al. illustrated, the irregular structure also caused the low melting enthalpy of the stereocomplex, because of the defective crystalline structure and irregular orientation of the lamellae. [53] Similary irregular, broken morphology was observed from samples containing different amount of PDLA by Yamane et al. and Schmidt et al. [25, 45]

2.4.5 Thermogravimetric Analysis

The purpose of this work was to detect the thermal degradation of PLLA, as well as the amount of residue solvent entrapped in dried samples. By ramp heating to 350 °C at 20 °C/min, and kept isothermally at 230 °C for 20 min (separately), the samples (unprocessed PLLA and PDLA pellets, and blends prepared by solution casting) were tested and the results were compared. All the samples were purged with nitrogen gas.

Fig. 2.30 shows the results obtained from TGA ramping experiment. The purpose of ramp heating test is to determine the onset point of weight loss because of thermal degradation.

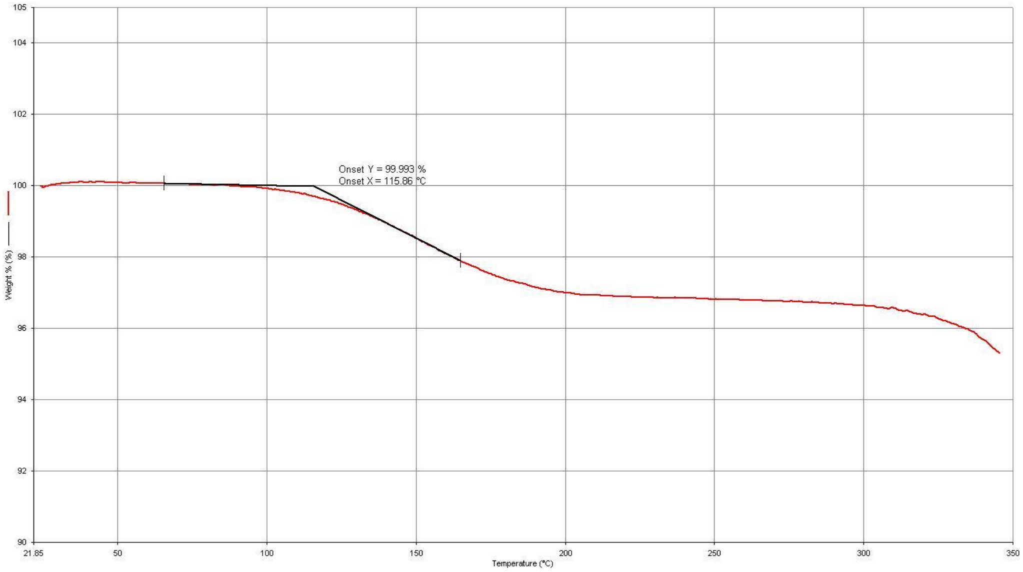
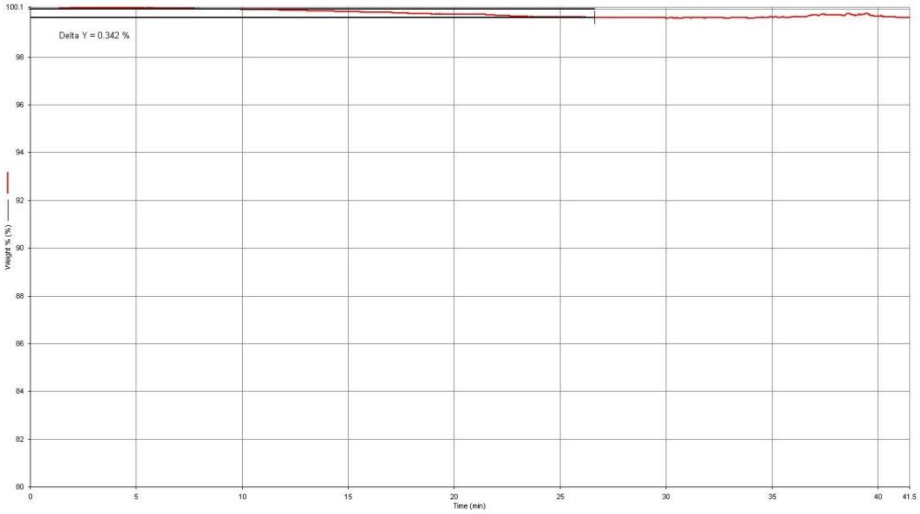


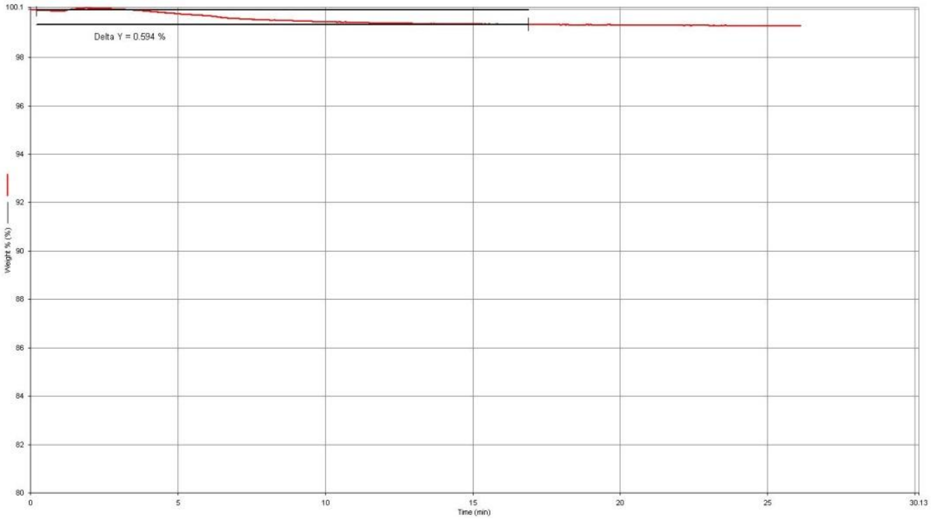
Fig. 2.30 TGA ramping curve from sample containing 15wt% PDLA.

The sample containing 15 wt% PDLA was used for the TGA ramp heating experiment. Before doing TGA analysis, the sample was dried in vacuum at 60 °C for 12 hours. As shown in Fig. 2.30, the weight loss onset temperature is 115.86 °C, and levels off at above 200 °C

In TGA isothermal analysis, the overall weight loss can be determined. Fig. 2.31 shows the isothermal experiment results from unprocessed PLLA and PDLA pellets, as well as the 15 wt% PDLA sample for previous ramp heating test.

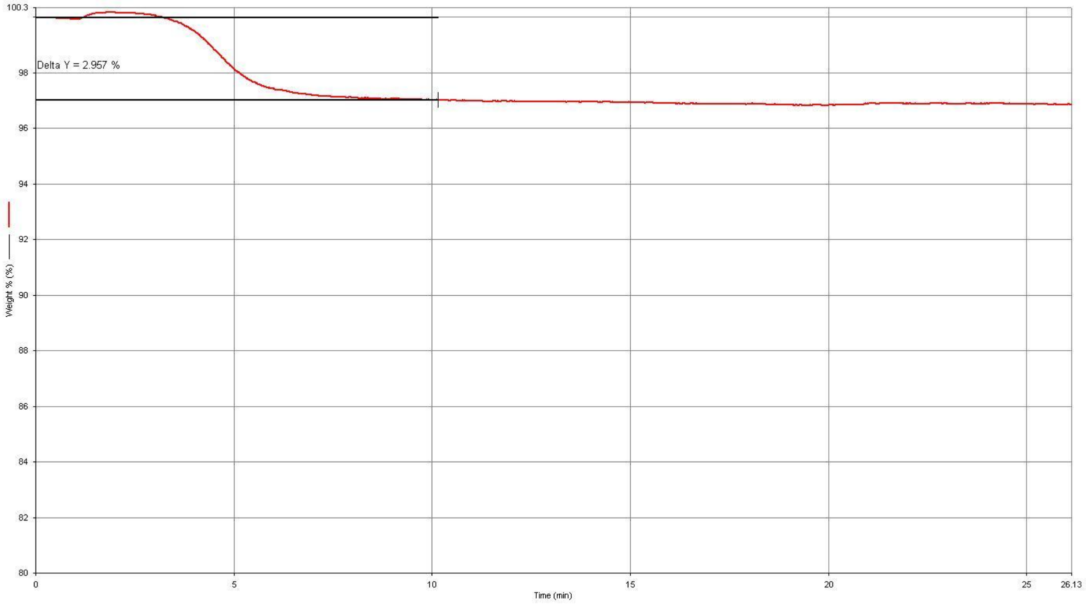


Unprocessed PLLA sample



Unprocessed PDLA sample

Fig. 2.31 TGA isothermal experiment results from unprocessed PLLA and PDLA pellets, and the 15 wt% PDLA sample.



15wt% PDLA sample

Fig. 2.31 (Coutinued) TGA isothermal experiment results from unprocessed PLLA and PDLA pellets, and the 15 wt% PDLA sample.

In TGA isothermal experiments, the samples were rapidly heated (40 °C/min) to 230 °C and held for 20 min. Shown in Fig. 2.31, the weight losses of unprocessed PLLA and PDLA samples are 0.342% and 0.594%, respectively. While in the sample containing 15 wt% PDLA, the weight loss is 2.976%, suggesting there was residual solvent entrapped in the material, after vacuum drying at 60 °C for 12 hours.

To verify this assumption, the same 15 wt% PDLA sample was re-dried in vacuum at 90 °C for 12 hours, and then tested with the same TGA isothermal program. The result is given in Fig. 2.32.

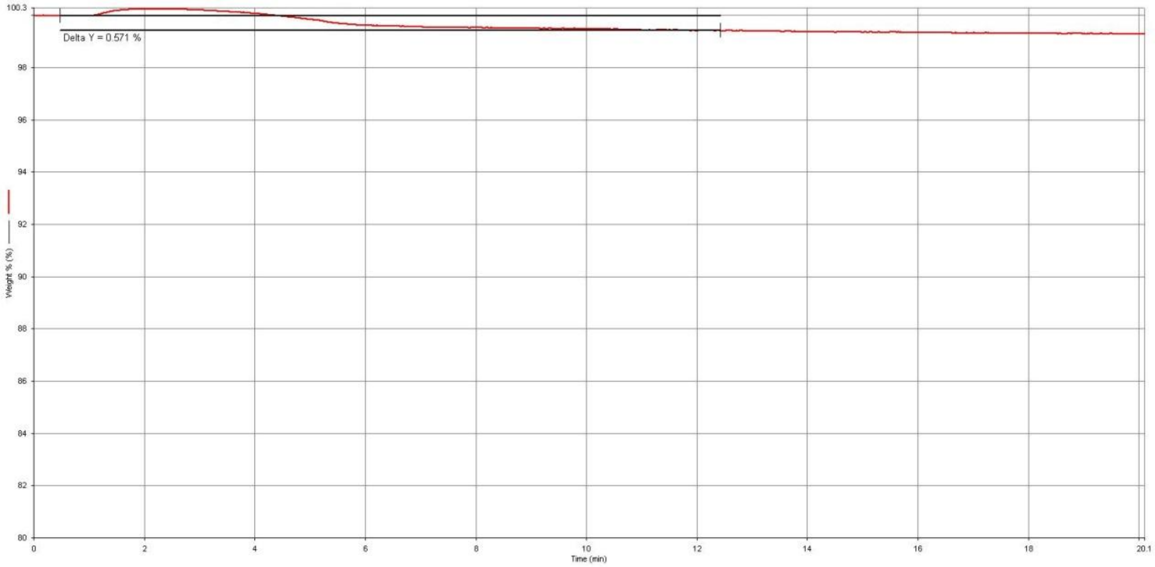
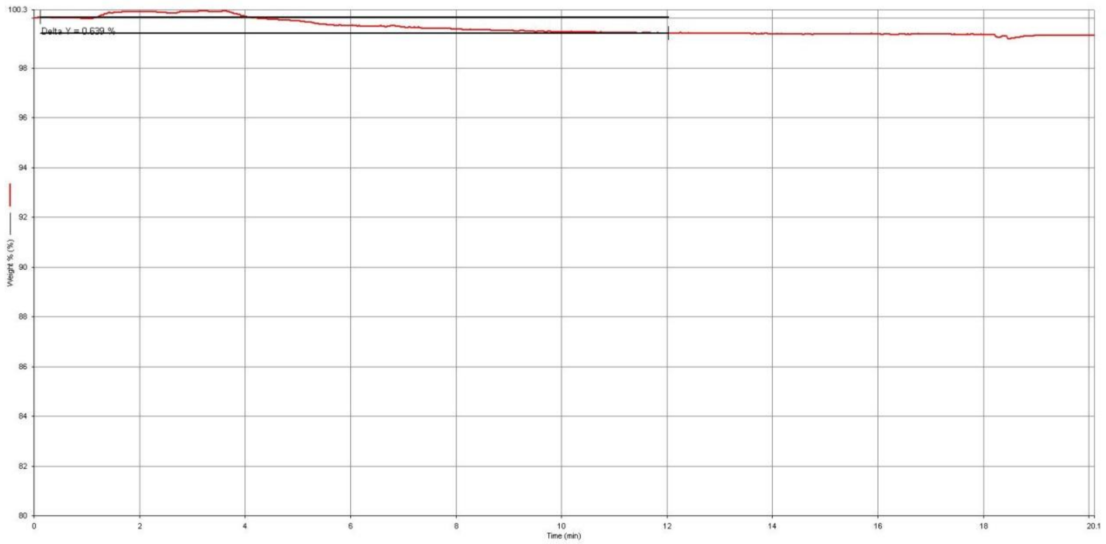


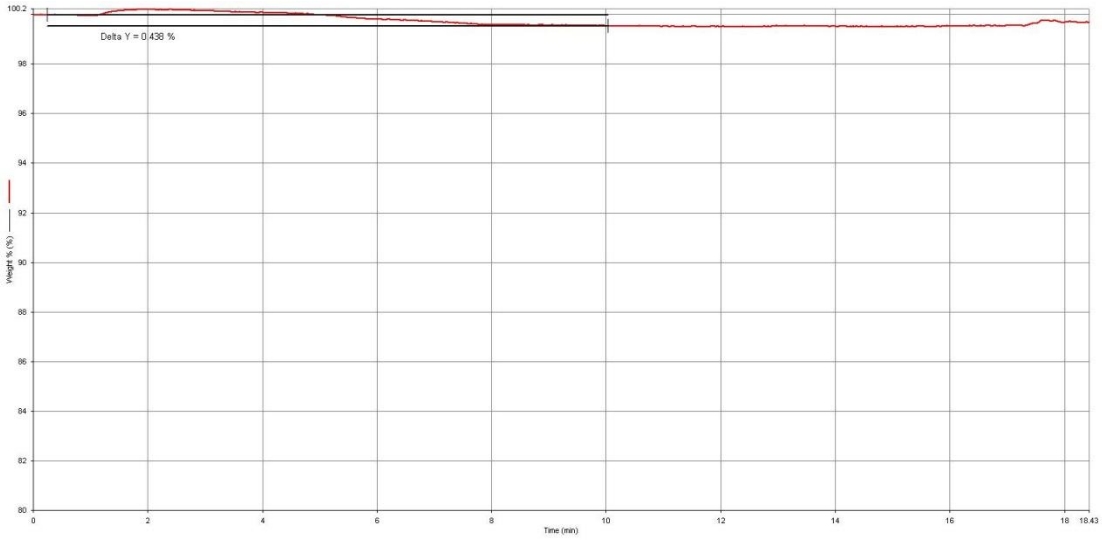
Fig. 2.32 TGA isothermal result from sample with 15 wt% PDLA, re-dried at 90 °C in vacuum for 12 hours.

Shown in Fig. 2.32, the weight loss of 15 wt% PDLA sample has gone down to 0.571%, which is in the same range as that of unprocessed PLLA and PDLA pellets. This result suggested that, if samples are kept in the vacuum at 90 °C for 12 hours, most of the residual solvent can removed.

After revising the drying method, newly made samples were tested with the same TGA isothermal program. The results confirmed that being held at 90 °C for 12 hours, the residue solvent in the samples can be mostly removed. Results are given in Fig. 2.33.



3wt% PDLA sample



15wt% PDLA sample

Fig. 2.33 TGA isothermal result from newly made samples containing 3 and 15 wt% PDLA, dried at 90 °C in vacuum for 12 hours.

In Fig. 2.33, the results again confirmed that the weight loss of samples dried in vacuum at 90 °C for 12 hours is in the same range as that of unprocessed PLLA and PDLA. Hence, this drying method was adopted for sample drying.

Additionally, to detect the influence brought by residue solvent, the DSC isothermal analysis results of original 15 wt% PDLA and re-dried 15 wt% PDLA were compared in Fig. 2.34. The results indicate that, the impact of 3% residue solvent on the thermal behavior of samples is undetectable.

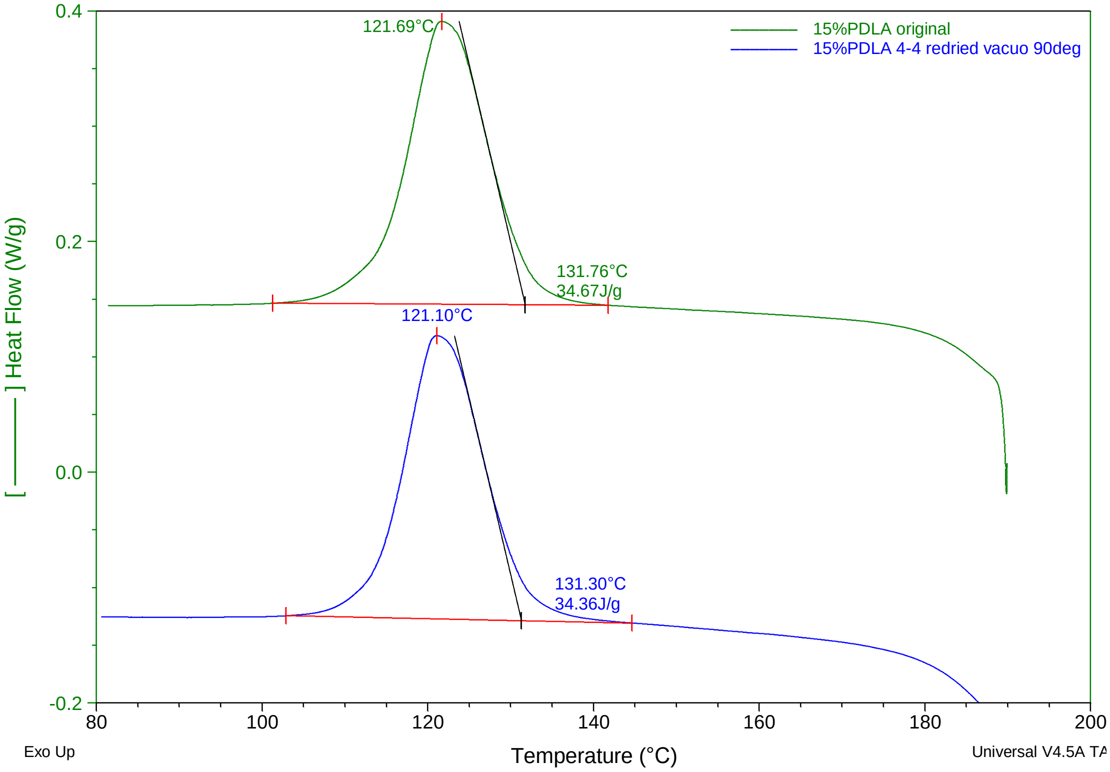


Fig. 2.34 Crystallization temperatures in the presence of stereocomplex, obtained from original 15 wt% PDLA sample and re-dried 15 wt% PDLA sample.

2.5 Further Discussion of Results

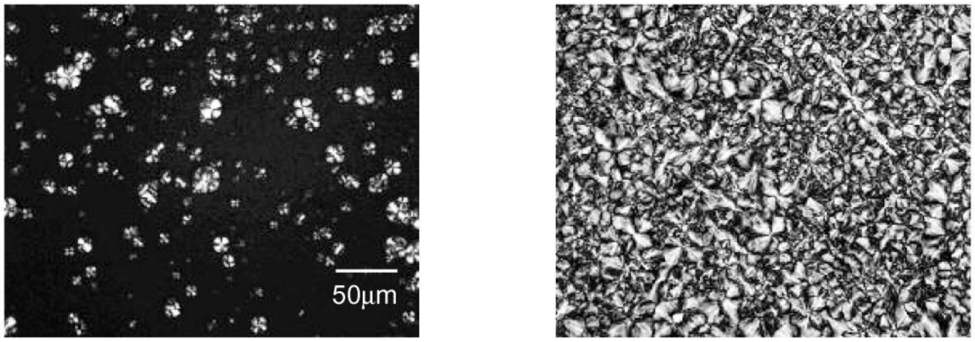
In the previous sections, the nucleating effect of PLLA/PDLA stereocomplex has been explained and confirmed. Through stereocomplexation, PLLA and PDLA can form a more stable stereo-structure, which provides stablized and flattened surface that possesses lower energy state at higher temperature, which neither PLLA nor PDLA homopolymers can do. The flattened surfaces then become crystallization sites for PLLA to grow epitaxially. With more stereocomplex in the system, the crystallization process can go faster and more extensively. This explains reason why the crystallization temperatures were elevated and the crystallization half-times were reduced, with increasing amount of PDLA.

It is recalled that in Fig. 2.27, the number of crystallites increased drastically with PDLA content. Yet in Fig. 2.17, it is shown that at 120 and 130 °C, the crystallization enthalpies from samples containing different amount of PDLA are nearly the same. To explain this phenomenon, the work done by Urayama et al. is referred here. By mixing talc with PLLA/PDLA matrix (1:1), they studied the nucleation effect brought by the additives. Table 2.6 gives the selected DSC data obtained from PLLA/PDLA their samples. Correspondingly, Fig. 2.35 gives the morphology changes brought by adding talc. [40]

Table 2.6 Selected DSC data of PLLA/PDLA with talc added [40]

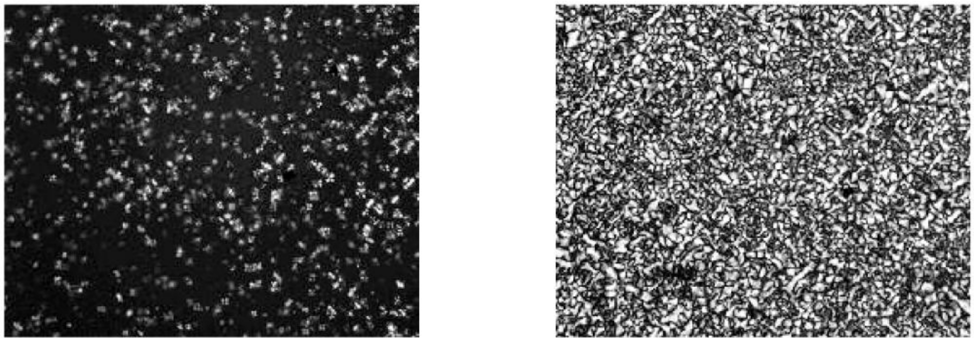
Polymer	Additive Content	T_c (°C)	Crystallization enthalpy (J/g)
PLLA/PDLA (1:1)	None	138.4	37.3
	Talc (1 wt%)	175	33.31
	Talc (2 wt%)	165.3	24.5

(a) PLLA/PDLA



150 °C 130 °C

(b) PLLA/PDLA+Talc



170 °C 150 °C

Fig. 2.35 Photomicrographs of (a) PLLA/PDLA, (b) PLLA/PDLA stereo mixtures with talc added (1 wt%) in the crystallization processes. [40]

As Urayama et al. described, in PLLA/PDLA sample without talc (Fig. 2.35 (a)), spherulites started to appear at 150 °C. At 130 °C, these spherulites were allowed to contact each other to cover the whole area, while small and imperfect crystallites were also detected in the dark amorphous regions among the large spherulites. In the presence of Talc, partial spherulites were formed (Fig. 2.35 (b)) having irregular shape which suggests the occurring of compositional fluctuation. However from Table 2.6, the crystallization enthalpies obtained from PLLA/PDLA samples with or without 1wt% talc do not fluctuate as much. [40] This resembling phenomenon discussed by Urayama et al.

may explain that the increasing amount of crystallites observed could not be reflected on the crystallization enthalpy obtained from DSC analysis. The crystallization enthalpy is an indication of well-formed, strong enough crystallites created during crystallization process. In this study, with more PDLA added, the increasing amounts of crystallites were more likely to have defective and irregular shape, instead of forming perfect spherulites. Thus the absence of well-formed spherulites could hardly contribute to the crystallization enthalpy.

Besides, recalling Fig. 2.7 and Fig. 2.9, the plateau of the melting enthalpy of stereocomplex was found with increasing PDLA content. To investigate whether more SC could be formed with increasing PDLA content, a sample containing 50 wt% PDLA was prepared. During sample preparation, after the PLLA and PDLA solutions (1 g/dL) were 1:1 combined and cast, the leftover mixture solution was sealed and kept at room temperature. The original intention of this step was to keep the solution as backup, in case that the dried film shows defect. Interestingly, with the film cast and dried from aforementioned solution, *3 days following preparation*, the DSC result showed no PLLA melting peak, but only a peak with 36.72 J/g melting enthalpy above 200 °C (Fig. 2.36). The sample was rapidly heated (100 °C/min) from 25 °C to 230 °C, and was held for 3 min for complete melting and to erase the thermal history. Then the sample was cooled (5 °C/min) from 230 °C to 80 °C, allowing the sample to crystallize. The blend was again heated from 80 °C to 230 °C, at 10 °C/min, to determine the melting temperatures. The corresponding morphology photomicrograph is shown in Fig. 2.37.

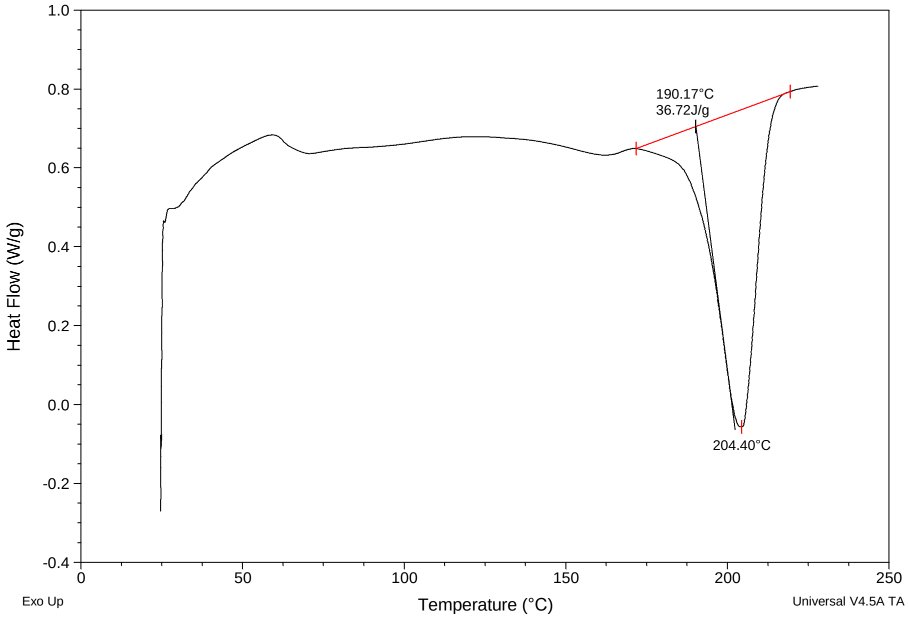


Fig. 2.36 DSC result from 50wt% PDLA blend sample.

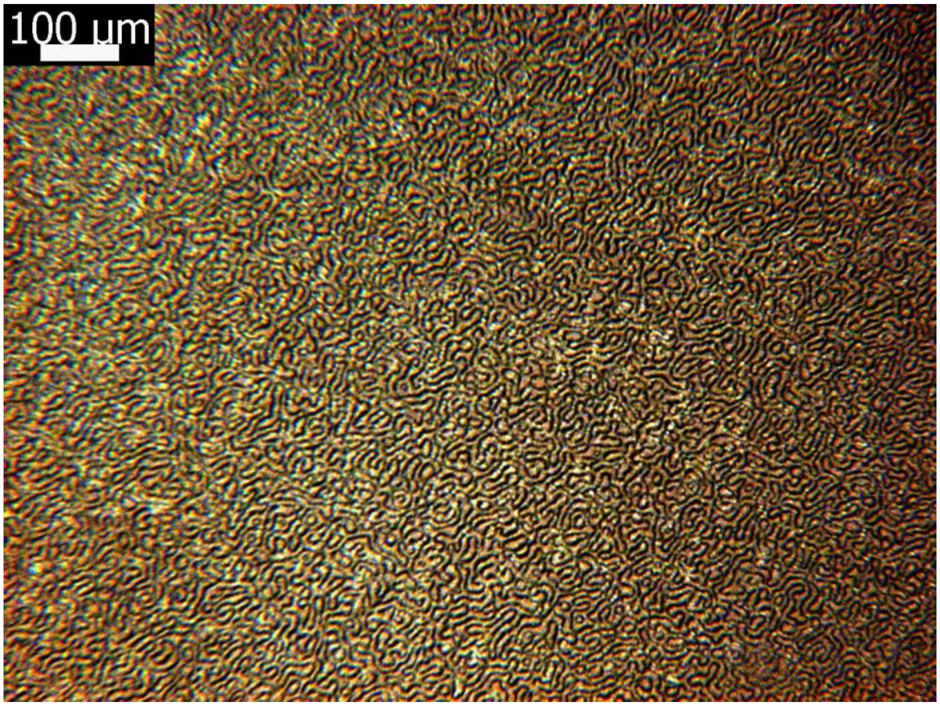


Fig. 2.37 Photomicrograph of 50 wt% PDLA blend sample.

During crystallization, the network structure shown in Fig. 2.37 started appearing around 160 °C, accompanied by few shiny specks, suggesting an irregular PLLA/PDLA stereocomplex structure was formed. Shown in Fig. 2.36, this structure has a melting point at 204 °C.

A similar DSC curve obtained from PLLA sample containing 50 wt% PDLA, in Tsuji et al.'s study, is given in Fig. 2.38. [16]

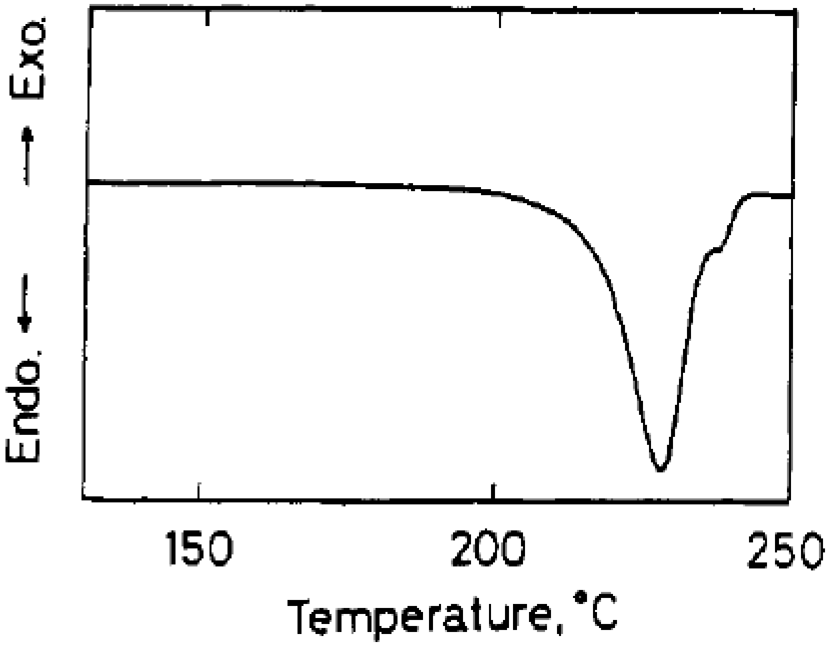


Fig.2.38 DSC melting curve of PLLA sample with 50 wt% PDLA. [16]

The sample tested in Tsuji et al.'s experiment was prepared as follows: Each of 10 g/dL (ten-fold higher than the 1 g/dL in the experiment here) chloroform solutions of PLLA and PDLA (both have M_w= 3.6×10^5 g/mol, similar to 3.4×10^5 g/mol in this study) were mixed and sealed in a test tube for 3 years at room temperature. Gelation took place and the gel became turbid in 3 years, suggesting the cross-liked or racemic crystallites were formed in the solution. Then after vacuum drying, the sample was examined by DSC, resulting in the single peak shown in Fig. 2.38, suggesting the successful stereocomplexation between PLLA and PDLA. As they explained, the racemic crystallites can be formed from a concentrated mixed PLLA and PDLA solution with aging. In contrast, they also prepared mixture sample with solution casting method (1 g/dL) with 1:1 low molecular weight PLLA and PDLA (4.9×10^3 g/mol), without aging, to detect whether the PLLA/PDLA complexation could take place. The result (Fig. 2.39, D1-L1) suggested the stereocomplex was successfully prepared. [16]

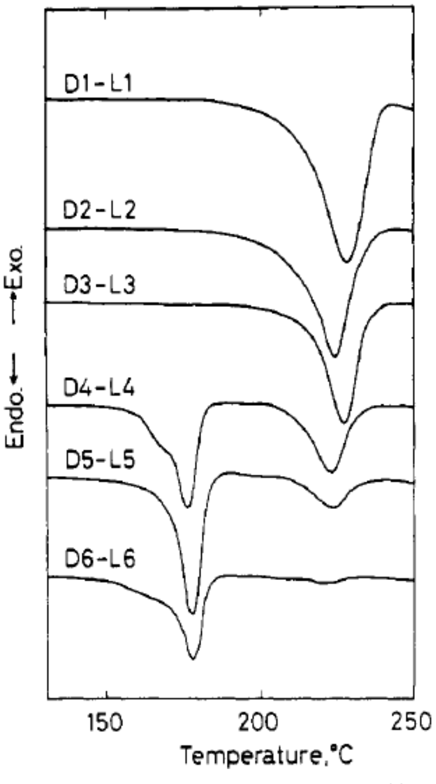


Fig.2.39 DSC results of 1:1 PLLA/PDLA samples with different M_w, without aging. [16]

Thus, comparing the DSC results from Tsuji et al.'s work and the DSC results in this study, the successful PLLA/PDLA complexation suggests that, with more PLDA incorporated, it will eventually form the stereocomplex by interacting with PLLA. So the plateau appeared in Fig.2.19 can be ascribed as the fact that the polymers with high molecular weight are hard to move, fold and tangle, comparing to that of low molecular weight polymers.

Theoretically, the polymer viscosity is inversely proportional to the chain mobility, while the viscosity is proportional to the molecular weight. The relation between viscosity and molecular weight can be explained by the following equations, [24]

$$\eta = K_L Z_w^{1.0} \tag{2-2}$$

$$\eta = K_H Z_w^{3.4} \tag{2-3}$$

here η is the polymer viscosity, Z_w is the number of atoms along the polymer chain's backbone. For PLA, Z_w = 2DP, DP is the degree of polymerization, representing the number of monomer units linked together, which is proportional to the molecular weight. K_L and K_H are constant for low and high degree of polymerization, having the same magnitude. When Z_w is smaller than 600, η has 1.0 power dependence on the molecular weight, and when Z_w is larger than 600, η has 3.4 power dependence on the molecular weight. [24] Knowing the molecular weight of PLA chain unit is 72 g/mol, Z_w of the polymers (D1 and L1) used in Tsuji et al.'s study (M_w = 4,900 g/mol) [16] and Z_w in this work (M_w = 340,000 g/mol) can be calculated as Z_w = 136 and Z_w = 9444, relatively. Thus the viscosity of PLA in this work ($\eta \sim 9444^{3.4}$) is extremely higher than that of Tsuji et al.'s study ($\eta \sim 136^{1.0}$), resulting in the extremely low chain mobility of PLA.

However, it is shown that, with longer time, PLLA and PDLA can interact extensively, so that more stereocomplex can be formed. This could also explain the phenomenon shown in Fig. 2.7, that in all the samples, the crystallization enthalpies of PLLA are way larger than that of stereocomplex. Due to the same short preparation time, the stereocomplexation did not extensively take place, causing the dominance of PLLA homocrystallization. This explanation is distinct from that in Tsuji et al.'s study, said that the tiny SC melting peak was caused by the phase-separation between high M_w PLLA and PDLA. It is noteworthy that, even with small amount of SC, their nucleating effect is highly noticeable.

CHAPTER 3

CONCLUSIONS

The nucleating effect of PLLA/PDLA stereocomplex was studied with samples containing different PDLA content (0, 0.3, 0.5, 1, 3, 5, 10, 15 wt%) prepared by dilute (5 g/dL) solution casting method. When crystallizing at 5 °C/min in the presence of stereocomplex, the crystallization temperature was elevated by 20 °C, compared to the T_c of pure PLLA. Under more rigorous crystallization conditions (15 and 25 °C/min cooling rate), the nucleation effect still can still be detected in samples containing higher PDLA content. During isothermal crystallization experiments, both the crystallization induction time and crystallization half-time were significantly shortened from 7 min to 1.5 min in the presence of stereocomplex at 120 and 130 °C. The fastest crystallization process was found in the sample containing 10 wt% PDLA. When crystallizing isothermally at 140 °C, significant amount of PLLA crystallites could still be induced with more than 3 wt% PDLA incorporated. Using hot stage polarized optical microscope, the nucleating effect brought by PLLA/PDLA stereocomplex was visually confirmed. With the Avrami equation (1-2), the isothermal crystallization kinetics was investigated. The observed non-spherulitic morphology could explain why the Avrami exponent (*n* values) calculated from samples containing varying PDLA content in this study were different from the theoretical *n* value for spherulite growth. With the accepted model, the nucleation efficiency for different samples was calculated. Moreover, the leveled-off nucleating effect was explained by the hindered formation of stereocomplex, because of the poor mobility caused by the high molecular weight of PLLA and PDLA.

CHAPTER 4

FUTURE WORK

From this study, the nucleating effect brought by the PLA stereocomplex has been confirmed. Even with high molecular weight (M_w = 340,000 g/mol), the PLLA and PDLA polymers could still form the stereocomplex, providing a significant enhancement on elevating PLLA crystallization temperature, as well as expediting the overall crystallization process. From self-nucleation theory, it is known that with nuclei of similar chemical constituent, the crystallization process can be greatly promoted. Thus other than comparing the T_c elevated by PLA, with T_c obtained from self-nucleation, the comparison of crystallization mechanism and kinetics should be conducted. With the isothermal crystallization parameters G (crystallization growth rate), $t_{1/2}$ (crystallization half-time), and the equation from Hoffman-Lauritzen theory [50],

$$\mathrm{G} = G_0 \exp\left[-\frac{U^*}{R(T_c - T_\infty)}\right] \exp\left[-\frac{K_g}{T_c \Delta T f}\right]] \qquad (4\text{-}1)$$

three regimes of crystallization can be determined. Here T_c is the isothermal crystallization temperature, U^* is the activation energy having value of 1500 cal/mol, R is gas constant, G is crystallization rate, $T_\infty = T_g$-30K, $f = 2T_c/T_m+T^0_m$, and K_g is the value of nucleation constant. With the similar derivation applied on Avrami equation (1-2), the equation above can be written in the following form:

$$\ln\mathrm{G} + \frac{U^*}{R(T_c - T_\infty)} = lnG_0 - \frac{K_g}{T_c \Delta T f} \qquad (4\text{-}2)$$

thus K_g can be calculated by plotting $lnG + \frac{U^*}{R(T_c - T_\infty)}$ versus $\frac{1}{T_c \Delta T f}$. The changes of K_g indicate the change of crystallization regime, showing the favorable crystallization temperature range. By comparing the calculation results from self-nucleation crystallization and crystallization with PLA stereocomplex, it may suggest that the crystallization mechanism of self-nucleation crystallization and the mechanism of crystallization with stereocomplex are similar, because of the similarity of the chemical constituent between stereocomplex and PLLA. Thus the PLA stereocomplex could be an ideal nucleating agent for PLLA.

On the other hand, in the previous chapter, the overall unchanged degree of crystallinity of PLLA is observed, which may be attributed to the insufficient amount of formed stereocomplex, caused by the poor chain mobility of high molecular weight PLLA and PDLA. Due to this reason, the improvement of thermomechanical properties may not be expected. As Tsuji et al. have found that the formation of stereocomplex could be promoted by using lower M_w PLA polymers. [16] The higher mobility may result in the ease of chain folding and rotating, leading the easier and more extensive stereocomplexation. Thus, with larger amount of PLA stereocomplex, the higher degree of crystallinity of PLLA may be achieved. Finally, the PLLA samples are expected to undergo the thermomechanical property experiments, to detect the increase of heat deflection temperature.

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