

To the Graduate Council:

I am submitting herewith a dissertation written by Xiaoyun Ling entitled “Thermal and X-ray Analysis on the Origin of Double Melting Phenomena of Poly(L-lactic acid) Films”. I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Polymer Engineering.

Joseph E. Spruiell
Major Professor

We have read this dissertation and
recommend its acceptance:

John R. Collier

Gajanan S. Bhat

Kevin M. Kit

Acceptance for the Council:

Anne Mayhew
Vice Chancellor and Dean of
Graduate Studies

(Original signatures are on file with official student records.)

**THERMAL AND X-RAY ANALYSIS ON THE ORIGIN
OF DOUBLE MELTING PHENOMENA OF
POLY(L-LACTIC ACID) FILMS**

A Dissertation
Presented for the
Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Xiaoyun Ling
December 2005

DEDICATION

This dissertation is dedicated to my dear husband, Kenneth M. Keilman,
best friend and soul mate.

ACKNOWLEDGEMENTS

I hereby wish to thank everyone who helped me complete my PhD degree in Polymer Engineering. I especially owe a great debt to my major advisor, Dr. Joseph Spruiell for his inspiration and guidance, as well as patience and support throughout this process. Sincere appreciation is also extended to my committee members: Dr. Gajanan Bhat, Dr. Kevin Kit and Dr. John Collier for sharing valuable insights and advice.

I would like to thank my former teacher Dr. Wenbing Hu, and Dr. Marek Pyda from ATHAS lab for great input from their knowledge and expertise in TMDSC.

I would like to thank our wonderful staff members: Sandy Maples, Carla Lawrence, Mike Neil, Frank Holiway, Randy Stooksbury, and Doug Fielden for all the administrative and technical assistance they provided. The cooperation from TANDEC members Van Brantley and Chris Eash, also from the PCL lab Tom Malmgren, will not be forgotten.

I would also like to thank my parents, Guoqing Ling and Yayuan Jiang, for their encouragement and support that have carried me further than I ever thought I would go. Special thanks goes to my lifelong best friends Jie Gao, Junlai Gao and Qing Ye, who have been good daughters to my parents when I am thousands of miles away.

Finally, I feel very grateful to my beloved husband, Kenneth M. Keilman, who is there for better and for worse, and gives me love and support without any conditions.

ABSTRACT

Thermal analysis is one of the most commonly used techniques to characterize the structure and properties of semicrystalline polymers. Unfortunately, the interpretation of thermal events is not always straightforward, but can be quite complicated. However, the complexity involved is often overlooked, leading to erroneous or, at least, questionable results and interpretations. In the present study we carry out an extensive investigation of the thermal behavior of poly(L-lactic acid), PLLA, films prepared under a wide range of crystallization conditions, including isothermal and non-isothermal crystallization from both the glassy state and the melt. The primary techniques used were differential scanning calorimetry (DSC), temperature modulated DSC (TMDSC), wide-angle x-ray diffraction (WAXD), and small angle x-ray scattering (SAXS). PLLA was known to exhibit complex thermal behavior, but there was disagreement in the literature about its interpretation. A major goal of the research was to sort out the various phenomena and to understand the mechanisms that produced them. This should provide a much better understanding of the thermal behavior of PLLA, but also would serve as an example of the complex behavior that can occur in semicrystalline polymers that could be useful in the interpretation of the results from other polymers.

Depending on the sample preparation conditions up to three crystallization peaks and two melting peaks could be observed during heating in the DSC. The occurrence of double melting is a function of crystallization temperature, crystallization time, heating rate, and molecular weight. It occurs under many experimental conditions, and it depends largely on the size and perfection of initial

crystals, not the overall initial crystallinity, nor the completion of crystallization. It was found that the first endotherm was often obscured due to the close competition between melting and recrystallization processes. In general, crystallization treatments performed at temperatures over 120°C for prolonged time periods eliminate the double melting behavior, suggesting that such treatments produce crystals of sufficient size and perfection that they do not readily recrystallize during heat-up in the DSC. Based on such observations it was concluded that double melting in PLLA originates mainly from the melt-recrystallization of metastable crystals. However, a proposal in the literature that double melting in PLLA is caused by the formation and subsequent transformation of a different, metastable phase, rather than the α -phase, at crystallization temperatures below 120°C could not be ruled out on the basis of our results.

A unique double “cold-crystallization” peak was observed when amorphous PLLA was heated at a rate of 10°C/min. It was concluded to result from the sum of conventional cold-crystallization and the melt-recrystallization of the unstable crystals formed during the initial cold-crystallization.

Analysis of our data to extract the equilibrium melting temperature, T_m^0 , and the equilibrium heat of fusion, ΔH_m^0 , was also carried out. These are very important quantities whose values vary widely in the literature. Our results indicate that $T_m^0 = 207 \pm 3^\circ\text{C}$ and $\Delta H_m^0 = 90 \pm 4 \text{ J/g}$. These values are comparable to some of the existing literature results.

TABLE OF CONTENT

CHAPTER 1	INTRODUCTION	1
CHAPTER 2	LITERATURE REVIEW	3
2.1	Overview of Poly(Lactic Acid)	3
2.2	Cold Crystallization and Double Cold Crystallization	8
2.3	Multiple Melting Peak Phenomena in Polymeric Materials.....	9
2.3.1	Poly(ether ether ketone) – PEEK – a semi-flexible polymer	9
2.3.2	Other semi-flexible polymer.....	24
2.3.3	Polypropylene – PP – a flexible polymer	26
2.3.4	Dual melting behavior of PLA	32
2.4	Equilibrium Heat of Fusion, $\Delta H_m(T_m^0)$ and Melting Temperature, T_m^0	36
2.4.1	Equilibrium heat of fusion, $\Delta H_m(T_m^0)$	36
2.4.2	$\Delta H_m(T_m^0)$ of PLLA.....	39
2.4.3	Equilibrium melting temperature, T_m^0	40
2.4.4	T_m^0 of PLLA.....	42
CHAPTER 3	MATERIALS AND EXPERIMENTAL METHODS	44
3.1	Materials	44
3.2	Crystallization and Partial Melting Processes	47
3.2.1	Crystallization from the glassy state (cold-crystallization)	47
3.2.2	Crystallization from the melt (melt-crystallization).....	47
3.2.3	Partial melting	48
3.3	Differential Scanning Calorimetry (DSC).....	49
3.4	Temperature Modulated DSC (TMDSC)	50
3.5	Thermogravimetric Analysis (TGA)	52
3.6	Dynamic Mechanical Analysis (DMA).....	52
3.7	Small Angle X-ray Scattering (SAXS) and Wide Angle X-ray Diffraction (WAXD).....	53
3.8	Gel Permeation Chromatography (GPC).....	54
3.9	Density Gradient Column (DGC).....	54

CHAPTER 4	SAMPLES CRYSTALLIZED FROM GLASSY STATE	56
4.1	Non-isothermal Crystallization from the Glassy State	56
4.2	Isothermal Crystallization from the Glassy State	63
4.2.1	Samples crystallized at different temperature for 1 hr	63
4.2.2	Samples crystallized at 80°C for different period of time	75
4.2.3	Heating rate effect on samples crystallized at 100°C and 120°C for 1 hr	81
4.2.4	Molecular weight effects on the double melting of PLLA.....	87
4.2.5	Partial melting of samples crystallized at 100°C for 1 hr.....	91
4.3	Summary.....	97
CHAPTER 5	SAMPLES CRYSTALLIZED FROM THE MELT	99
5.1	Non-isothermal Crystallization from the Melt	99
5.1.1	Samples crystallized at different cooling rate	99
5.1.2	Heating rate effect on double melting of non-isothermally crystallized samples	104
5.2	Isothermal Crystallization from the Melt	112
5.2.1	Samples crystallized at different temperatures for 1 hr.....	112
5.2.2	Samples crystallized at 140°C for different period of time	118
5.3	Summary.....	122
CHAPTER 6	ESTIMATION OF EQUILIBRIUM MELTING TEMPERATURE AND HEAT OF FUSION OF PERFECT CRYSTAL	126
6.1	Gibbs-Thomson Method for Equilibrium Melting Temperature, T_m^0	126
6.2	Hoffman-Weeks Method for Equilibrium Melting Temperature, T_m^0	126
6.3	Flory Method for Equilibrium Melting Temperature, T_m^0	129
6.4	Specific Volume Method for Equilibrium Heat of Fusion, ΔH_m^0	130
6.5	Flory Method for Equilibrium Heat of Fusion , ΔH_m^0	131
6.6	Summary.....	135
CHAPTER 7	SUMMARY AND CONCLUSIONS.....	137
CHAPTER 8	FUTURE RESEARCH	141
LIST OF REFERENCES.....		142
VITA		153

LIST OF TABLES

Table 4.1 Summary of Observed Thermal Effects of PLLA Cold-crystallized at Different Temperatures for 1 hr (°C) and the Degree of Crystallinity	66
Table 4.2 Lorentz Corrected Long Period and Lamellae Thickness of PLLA Cold-crystallized at Different Temperatures for 1 hr	74
Table 4.3 Summary of Observed Thermal Effects of PLLA Cold-crystallized at 80°C for Different Period of Time (°C) and the Degree of Crystallinity.....	77
Table 4.4 Glass Transition, Cold-crystallization and Melting Temperatures of PLLA Amorphous Samples with Different Molecular Weights	90
Table 4.5 Summary of Observed Thermal Effects PLLA-CC100-60min Partially Crystallized at Different Temperature (°C) and the Degree of Crystallinity.....	93
Table 4.6 Long Period and Lamellar Thickness of PLLA-CC100-60min Partially Melted at Different Temperatures	95
Table 5.1 Crystallization Temperature, Crystallinity, Long Period, Lamellar Thickness of Non-isothermal Melt-crystallized PLLAs from Different Cooling Rates.....	100
Table 5.2 The Occurrence of Double Melting Peaks in the Subsequent Heating Scans of Non-isothermally Melt-crystallized PLLAs at Different Cooling Rates	104
Table 5.3 Summary of Observed Thermal Effects of PLLA Melt-crystallized at Different Temperatures for 60 Minutes (°C) and the Degree of Crystallinity...	114
Table 5.4 Long Period and Lamellar Thickness of PLLA Melt-crystallized at Different Temperatures for 60 minutes.....	119
Table 5.5 Summary of Observed Thermal Effects of PLLA Melt-crystallized at 140°C for Different Period of Time (°C) and the Degree of Crystallinity.....	121
Table 5.6 Lorentz Corrected Long Period and Lamellar Thickness of PLLA Melt-crystallized at 140°C for Different Period of Time	124
Table 6.1 Characteristic Data of the Lactide Copolymers, Data of Fischer et al. ¹¹⁵ .	133
Table 6.2 Equilibrium Heat of Fusion and Melting Temperature Calculated from the Slopes and Intercepts of Curves in Figure 6.7 and 6.8	135

LIST OF FIGURES

Figure 2.1 Polymerization Schemes of Lactic Acids ⁹	3
Figure 2.2 Enantiomeric Forms of Lactic Acids and Lactides ¹⁰	4
Figure 2.3 Wide Angle X-ray Scattering Patterns of (A) Experimental ¹⁶ and (B) Simulated ¹² PLA Fibers with (1) α - and (2) β -crystals.....	6
Figure 2.4 Typical DSC Curve of Amorphous PLLA Film, 10°C/min.....	9
Figure 2.5 Chemical Structure of Poly(ether ether ketone) (PEEK)	10
Figure 2.6 Heat of Fusion (left) and Melting Peak Temperatures (right) vs. Heating Rate. ⁵⁴ (The PEEK samples were cold-crystallized at 220°C for 75 hrs.).....	13
Figure 2.7 Melting Peak Temperatures vs. Heating Rate ⁵⁴ (The PEEK samples were melt-crystallized at -▲-322.8°C for 20 hrs and -○- 318.6°C for 14 hrs.)	13
Figure 2.8 Schematic Representation of the Melting Mechanism Proposed for (A) Poly(ϵ -caprolactone), Adapted from Rim and Runt ⁷⁵ and (B) PEEK (M represents the melting endotherm of the original crystals; the dotted lines represent the recrystallization exotherm and the melting endotherm of the recrystallized crystals; the shaded area in B represents melting of the core crystalline region) ⁵⁴	15
Figure 2.9 Long Period versus Crystallization Temperature for Cold-crystallized and Annealed PEEK ⁵⁵	17
Figure 2.10 TMDSC Thermograms of Isothermally Melt-crystallized PEEK at (A) 290°C and 300°C, (B) 310°C and 320°C for 10 minutes ⁷⁶	17
Figure 2.11 Peak Temperatures of T _m I (○,●) and T _m II (□,■) versus Heating Rate for Samples Prepared at 280°C (filled symbols) and 340°C (open symbols) ⁵⁸	19
Figure 2.12 Heating Rate Effect of PEEK (A) Melt-crystallized at 310°C for 1h ⁸⁰ and (B) Annealed at 320°C for 1h ⁵⁵	20
Figure 2.13 PEEK Melt-crystallized from 310°C for Different Time. (A) Cooled to 200°C and Rescanned; (B) Scanned Directly from the Crystallization Temperature ⁸⁰	21

Figure 2.14 Two Types of Long Period (L_B and L_C^M) and Lamellar Thickness versus Temperature ⁶⁴	23
Figure 2.15 Schematic Representation of the Melting Mechanism for the Dual Lamellar Thickness Model (the thinner shaded bars represent the secondary lamellae and the thicker ones represent the primary lamellae which are subsequently thickened) ⁶⁴	24
Figure 2.16 Optical Micrographs of iPP Samples Isothermally Melt-crystallized at 128°C. (A) Showing α - and β -spherulites and (B) Showing Separate Melting of β -spherulites. ⁹⁶	27
Figure 2.17 Scanning Electron Micrographs (left), X-ray Diffraction Patterns (middle) and DSC Thermograms (right) of iPP Plate Obtained for Samples Taken from (a) the Surface Region; (b) the Core Region ⁹⁷	29
Figure 2.18 DSC Melting Scans at 10°C/min for iPP Sample that (A) Crystallized at 148°C and (B) Crystallized at 148°C and Subsequently Subjected to the Etching Procedure. ¹⁰²	30
Figure 2.19 DSC Thermogram for Melt-crystallized iPP at 111°C, Effect of Heating Rate, Curve A, B, C, and D are for Heating Rate of 2,4,8,16°C/min ¹⁰⁵	31
Figure 2.20 DSC Thermograms for (A) Amorphous PLA40 and Samples Treated in the DSC up to (B) 95°C, (C) 110°C, and (D) 150°C ¹¹⁶	34
Figure 2.21 CR-HR Map of the Appearance of Double Melting Peaks of PLLA (-●- double melting peaks and -□- single melting peak) ¹²²	34
Figure 2.22 Wide-angle X-ray Diffraction Patterns of Various Samples: (a) As-prepared, Amorphous PLLA, (b) By One-step Annealing at 90°C for 20 min, (c) By One-step Annealing at 160°C for 1 h, (d) By Two-step Annealing (the first step at 90°C for 20 min, and the second step at 160°C for 10 min), and (e) Melt-crystallized by Ambient Cooling from Melt at 200°C. ¹²³	35
Figure 2.23 Apparent Melting Temperature vs. Inverse Lamellar Thickness of PLA Crystallized at Different Temperature ¹³¹	40
Figure 2.24 T_m^{-1} vs. M_n^{-1} for PLLA ⁴⁰	41

Figure 2.25 The Melting Temperature of PLLA as a Function of the Crystallization Temperature from DSC, 5°C/min ³²	43
Figure 2.26 The Melting Temperature of PLLA as a Function of the Crystallization Temperature from DSC, 8°C/min, 5°C/min, 4°C/min from Top ³³	43
Figure 3.1 WAXD of Amorphous PLLA Film	44
Figure 3.2 DSC Thermograms of Raw and Amorphous Films of PLLA, 10°C/min ...	46
Figure 3.3 DSC Thermograms of Raw and Amorphous Films of PLLA-C, 10°C/min	46
Figure 3.4 DSC Thermogram of PLLA-CC100-60min, Partial Melting Performed Where Marked (a) 120°C (b) 130°C (c) 140°C (d) 150°C (e) 155°C (f) 160°C (g) 165°C (h) 170°C (i) 175°C	48
Figure 3.5 Calibration Curve of the Density Gradient Column for PLLA.....	55
Figure 4.1 DSC Thermograms of Amorphous PLLA Film Scanned at Different Heating Rates.....	56
Figure 4.2 Total, Reversing, Non-reversing Heat Flow of Amorphous PLLA Film vs. Temperature at 1°C/min, with 0.5°C Amplitude and 60s Period from TMDSC .	58
Figure 4.3 Reversing Heat Flow vs. Temperature from Figure 4.2	58
Figure 4.4 DMA of PLLA Amorphous Fil at 1°C/min Ramp and 1Hz Frequency in Tensile Mode	60
Figure 4.5 Crystallization Rate vs. Crystallization Temperature of PLLA Amorphous Film.....	61
Figure 4.6 TGA Thermogram of PLLA Amorphous Film and Its First Derivative.....	62
Figure 4.7 DSC Thermograms of Isothermally Cold-crystallized Samples with Different Procedures (Procedure I: heating from 25°C to 200°C after quenching, and Procedure II: heating directly from T _{cc} to 200°C, at 10°C/min. From top to bottom, T _{cc} is 90°C, 110°C, 130°C and 150°C)	63
Figure 4.8 DSC Thermograms of PLLA Cold-crystallized at Different Temperature for 60 minutes, 10°C/min	65
Figure 4.9 Major Melting Temperature as a Function of Cold-crystallization Temperatures of Cold-crystallized PLLAs.....	69

Figure 4.10 WAXD Patterns of PLLA Cold-crystallized at Different Temperature for 60 minutes.....	71
Figure 4.11 Lorentz Corrected SAXS of PLLA Cold-crystallized at Different Temperature of 60 minutes.....	74
Figure 4.12 Long Period and Crystalline Thickness as a Function of Cold Crystallization Temperature of Cold-crystallized PLLAs.....	75
Figure 4.13 DSC Thermograms of PLLA Cold-crystallized at 80°C for Different Period of Time, 10°C/min	76
Figure 4.14 WAXD Patterns of PLLA Cold-crystallized at 80°C for Different Period of Time	78
Figure 4.15 SAXS Patterns of PLLA Cold-crystallized at 80°C for Different Period of Time.....	79
Figure 4.16 DSC Thermograms of PLLA Cold-crystallized at 108°C for 15, 120 and 600 minutes.....	80
Figure 4.17 DSC Thermograms of PLLA Cold-crystallized at 110°C for 60, 240 and 600 minutes.....	80
Figure 4.18 DSC Thermograms of PLLA-CC100-60min Scanned at Different Heating Rate	82
Figure 4.19 Selected Individual DSC Thermograms of PLLA-CC100-60min Subject to (a) 2.5°C/min, (b) 20°C/min, (c) 50°C/min, and (d) 80°C/min Heating Rate ...	83
Figure 4.20 DSC Thermograms of PLLA-CC120-60min Scanned at Different Heating Rate.....	85
Figure 4.21 Selected Individual DSC Thermograms of PLLA-CC120-60min Subject to (a) 1°C/min, (b) 2.5°C/min, (c) 5°C/min, and (d) 10°C/min Heating Rate	86
Figure 4.22 Molecular Weight (GPC) and Mass (TGA) Changes for PLLA Held at 210°C for Different Period of Time	89
Figure 4.23 DSC Thermograms of PLLA with Different Molecular Weights.....	89
Figure 4.24 DSC Thermograms of PLLA-CC100-60min Partially-Melted at Different Temperature.....	92

Figure 4.25 WAXD Patterns of PLLA-CC100-60min Partially-Melted at Different Temperatures	94
Figure 4.26 Lorentz Corrected SAXS of PLLA-CC100-60min Partially Melted at Different Temperatures.....	95
Figure 4.27 Lamellar Long Period as a function of Partial Melting Temperatures of PLLA-CC100-60min	96
Figure 5.1 DSC Thermograms of Non-isothermal Melt-crystallization of PLLA at Different Cooling Rates.....	100
Figure 5.2 WAXD Patterns of Non-isothermally Melt-crystallized PLLA at Different Cooling Rates	102
Figure 5.3 Crystalline and Amorphous Thickness of PLLA Melt-crystallized Non-isothermally at Different Cooling Rates.....	103
Figure 5.4 DSC Heating Scans at Different Heating Rates after Non-isothermal Melt-crystallized at 0.5°C/min.....	105
Figure 5.5 DSC Heating Scans at Different Heating Rates after Non-isothermal Melt-crystallized at 1°C/min.....	106
Figure 5.6 Individual DSC Thermographs of (a) PLLA-CR1+HR1, (b) PLLA-CR1+HR5, and (c) PLLA-CR1+HR10 with Baselines	107
Figure 5.7 DSC Heating Scans at Difference Heating Rates after Non-isothermal Melt-crystallization at 3°C/min	109
Figure 5.8 DSC Thermograph of PLLA-CR3+HR30	109
Figure 5.9 Second DSC Heating Scan at Difference Heating Rate after Cooling Down from the Melt at 10°C/min.....	110
Figure 5.10 DSC Thermograms of PLLA Melt-crystallized at Different Temperatures for 60 minutes, 10°C/min	113
Figure 5.11 Major Melting Temperatures as a Function of Isothermal Melt-crystallization Temperatures of PLLAs.....	116
Figure 5.12 WAXD Patterns of PLLA Melt-crystallized at Different Temperature for 60 minutes.....	117

Figure 5.13 Lorentz corrected SAXS of PLLA Melt-crystallized at Different Temperature for 60 minutes	119
Figure 5.14 DSC Thermograms of PLLA Melt-crystallized at 140°C for Different Period of Time, 10°C/min	120
Figure 5.15 DSC Thermogram of PLLA-MC140-75min.....	121
Figure 5.16 WAXD Patterns of PLLA Melt-crystallized at 140°C for Different Period of Time	123
Figure 5.17 Lorentz Corrected SAXS of PLLA Melt-crystallized at 140°C for Different Period of Time	124
Figure 6.1 Apparent Melting Temperature vs. Inverse Lamellar Thickness of PLLA Melt- and Cold-crystallized at Different Temperatures	127
Figure 6.2 The Apparent Melting Temperature of PLLA as a Function of the Melt Crystallization Temperature from DSC, 10°C/min	128
Figure 6.3 The Apparent Melting Temperature of PLLA as a Function of the Cold Crystallization Temperature from DSC, 10°C/min	129
Figure 6.4 $1/T_m$ vs. $1/M_n$ for PLLA.....	130
Figure 6.5 Heat of Fusion as a Function of Specific Volume for Samples that are Non-isothermally Cold-crystallized at Different Cooling Rates	131
Figure 6.6 Plot of $1/T_m I$ vs. $\ln X_L$ for the Single Crystals Obtained at 20°C Supercooling ¹¹⁵	133
Figure 6.7 Plot of $1/T_m I$ vs. $\ln X_L$ for the Single Crystals Obtained at 20°C and 9°C Supercooling Using Fischer et al.'s Data ¹¹⁵	134
Figure 6.8 Modified Plot of $1/T_m I$ vs. $\ln X_L$ for the Single Crystals Obtained at 20°C and 9°C Supercooling Using Selected Fischer et al.'s Data ¹¹⁵	134

CHAPTER 1 INTRODUCTION

As unprecedented global environmental awareness is calling for the reduction of environmental hazards, biodegradable polymers are gaining considerable attention. Poly(lactic acid), or PLA, is one of the most promising biodegradable/biocompatible polymers to answer the challenge.

Lactic acid is essentially derived from annually renewable agriculture resources such as corn, rice, wheat, sugar beet, etc. Dextrose extracted from the starch is fermented to produce lactic acid, a common food ingredient and monomer for PLAs. When PLA degrades, it first breaks down to lactic acid and finally to carbon dioxide, water and biomass. It comes from nature and goes back to nature, thus very environmental friendly. The normal degradation time of PLAs are on the order of six months to two years, with ten years (pure PLLA) as upper limit, compared to 500 to 1000 years for PS and PE ¹. In the past, PLA was exclusively used in biomedical applications such as surgical sutures, bone fixation devices and drug delivery systems due to high cost of raw material. As polymer production surges over the last few years (thanks to the combined effort of Cargill and Dow), the price has dropped substantially to the level that commercial interest to substitute conventional petroleum-based thermoplastic with PLA is rising dramatically. Nowadays, fibers for garments and carpets, films for industrial and agricultural usages, nonwovens for disposable products such as diapers ², and beyond are being developed in research labs, pilot lines and final production stages. A list of basic patents is made available by Linnemann ².

With such a remarkable potential of PLA and high demand of production market, broader and deeper understanding of the properties of PLAs beyond its biomedical scope becomes an immediate necessity. As a worldwide effort is contributing to this subject, our group has also been actively involved³⁻⁸.

As we know, the properties of a semicrystalline polymer depend greatly on its thermal history, so that a better understanding of its thermal behavior is essential to a clearer picture of property variations. Thermal behavior is often studied with differential scanning calorimetry (DSC) technique that is easy to operate. However, the interpretation of the DSC thermograms is usually more complex than imagined, e.g. debate has long existed on whether the multiple melting phenomena are induced by heating in DSC. Literature has shown different approaches in various systems, however, not much has been done in regard to PLA so far.

Our major objective is to investigate the origin of the double melting behavior of PLLA, and explore the relationship between the various crystallization/processing conditions and the occurrence of recrystallization, the success of which can also be beneficial to the development of industrial processing and the understanding of related properties such as warp, dimension stability, creep, soften on elevated temperature, etc. Moreover, during the course of this research, an unusual double cold-crystallization peak appeared during the heating of amorphous PLLA, is also examined. In addition, the equilibrium melting temperature, T_m^0 , and the equilibrium heat of fusion, ΔH_m^0 , will be evaluated in that considerable discrepancy exists in the literature.

CHAPTER 2 LITERATURE REVIEW

2.1 OVERVIEW OF POLY(LACTIC ACID)

PLAs, $(-\text{CHCH}_3-\text{CO}-\text{O}-)_n$, can be synthesized either by the polycondensation of lactic acid, or by ring-opening polymerization of lactide, a cyclic dimer of lactic acid, as illustrated in **Figure 2.1**. The latter generally yields high molecular weight products. Different synthesis tactics, though not covered due to the scope of this research, are discussed in greater detail in a recent review by Garlotta ¹.

Lactic acid has a chiral center, thus two enantiomeric L- and D- forms (**Figure 2.2**). Both forms are optically active. Accordingly, there exist four forms of lactides, namely, L-lactide, D-lactide, racemic D,L-lactide, and mesomorphic D,L-lactide. D,L-lactides are optically inactive. By maneuvering the compositions and chiralities of these forms, a range of PLAs can be produced to meet the requirements of various end-use applications.

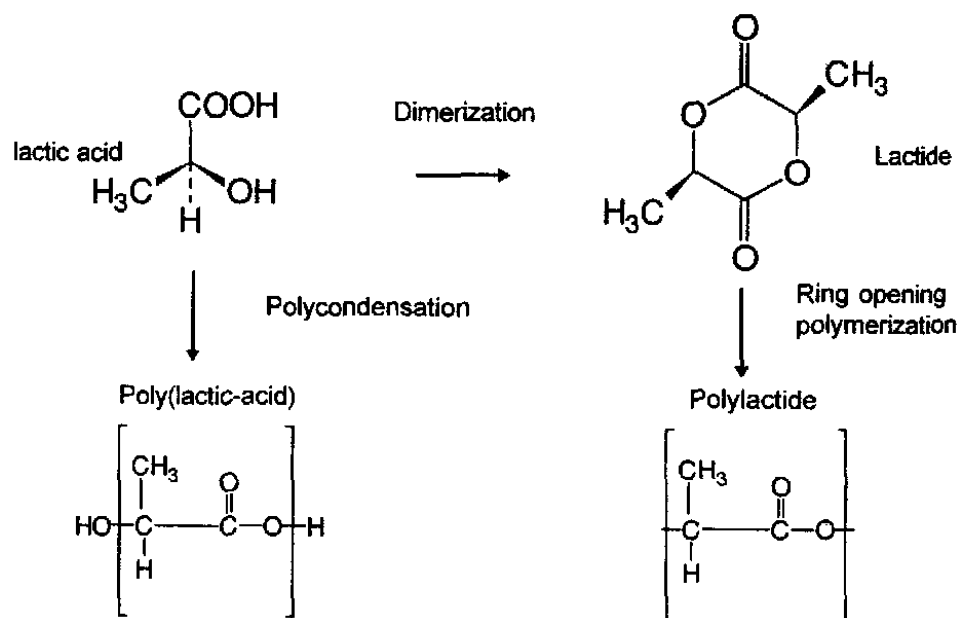


Figure 2.1 Polymerization Schemes of Lactic Acids ⁹

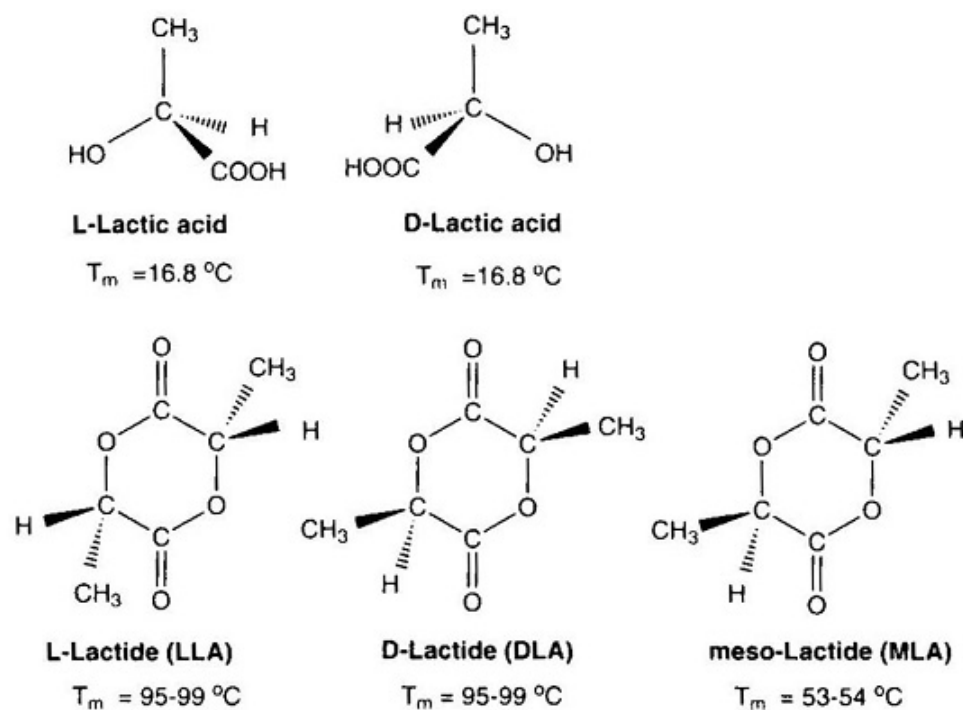


Figure 2.2 Enantiomeric Forms of Lactic Acids and Lactides ¹⁰

There have been many fundamental researches on crystal structures of PLA and three different crystal modifications were so far recognized. De Santis and Kovacs ¹¹ first reported the α -crystal for melt-spun fibers on the basis of x-ray diffraction pattern. The chain conformation was determined to be a left-handed 10₃ helix. The pseudo-orthorhombic unit cell of a=1.07nm, b=0.645nm and c=2.78nm includes two chains. Since then, this major PLA crystal structure has been extensively studied by different groups ¹²⁻¹⁶, reporting slightly different parameters. β -crystal was first revealed by Eling et al. ¹⁷ when solution-spun PLLA fibers are subjected to high draw ratio or temperature. However, no unit cell dimensions were provided. An orthorhombic unit cell of a=1.031nm, b=1.821nm and c=0.900nm containing six chains for the β -crystal was later proposed by Hoogsteen et al. ¹⁶. They also

concluded that the chain conformation of β -crystal is left-handed 3_1 helix, and α - and β -crystal bear folded-chain and fibrillar morphology, respectively. Based on molecular modeling, Brizzolara et al.¹² examined Hoogsteen et al.'s¹⁶ data and concluded the existence of two parallel chains instead of six in an orthorhombic unit cell of $a=1.060\text{nm}$, $b=0.605\text{nm}$ and $c=0.940\text{nm}$. **Figure 2.3** shows the experimental¹⁶ and simulated¹² x-ray patterns of α - and β - crystals. However, Puiggali et al.^{18, 19} suggested β -crystal being actually a “frustrated” structure, whose packing accommodates three (not two or six) 3_1 helices with random up-down orientation in a trigonal unit cell of parameters $a=b=1.052\text{nm}$ and $c=0.88\text{nm}$ and is associated with rapid crystallization conditions (stroking or stretching of the α -crystal). A new structure, γ -crystal, was recently observed only through epitaxial crystallization on hexamethylbenzene (HMB) by Cartier et al.²⁰. Two anti-parallel helices are packed in an orthorhombic unit cell of $a=0.995\text{nm}$, $b=0.625\text{nm}$ and $c=0.88\text{nm}$, the parameters of which are similar to that of β -crystal calculated by Brizzolara et al.¹². It was specifically pointed out by Puiggali et al.¹⁸ that the frustrated structure (or β -crystal) is formed when the regular pattern of antiparallel chain orientations characteristic of the γ -crystal cannot be established.

Equimolar PLLA and PDLA crystallize into racemic crystals, also known as stereocomplex. It exhibits a $T_m=230^\circ\text{C}$, which is almost 50°C higher than its enantiomeric counterparts (185°C for α - and 175°C for β -crystals) and possesses greater mechanical properties due to certain favorable Van de Waals interaction.

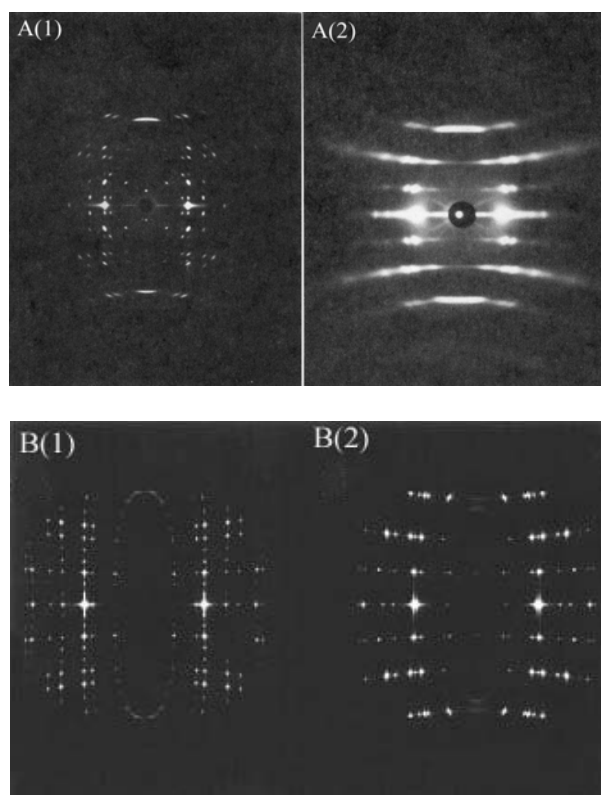


Figure 2.3 Wide Angle X-ray Scattering Patterns of (A) Experimental¹⁶ and (B) Simulated¹² PLA Fibers with (1) α - and (2) β -crystals

However, when one of the components of the stereocomplex has an optical purity of 80%, the corresponding T_m is only about 25°C higher²¹. Since the first communication of stereocomplex formation between enantiomeric poly(lactide)s by Ikada et al.²², a series of researches were then conducted by the same group²³⁻³¹ and other groups^{12, 21}. The stereocomplex was reported to crystallize in a triclinic system in which the unit cell dimension are $a=b=0.916\text{nm}$, $c=0.87\text{nm}$, $\alpha=\beta=109.2^\circ$ and $\gamma=109.8^\circ$ and to house two 3_1 helices of different enantiomeric species²³. It is quite different from the aforementioned structures of homopolymers. Even when it takes the β -crystal helices; the packing scheme of stereocomplex is very different. It is

suggested that the racemic crystals form through the packing of 3_1 helices (of opposite absolute configurations) alternating side by side ¹². Such arrangement could lead to the stabilization of the helices, which enhances overall stability of the stereocomplex ¹². In addition, the uncommon triangular shape often exhibited in single crystals of poly(lactide) stereocomplex ^{12, 19, 23} is possibly due to the imbalanced growth rate of the right- and left-handed helices onto the opposite side of the growth plane ¹⁹.

Crystallization behavior of PLLA from solution ³² and from melt ³³⁻³⁸ have been studied by hot stage microscopy ³³, DSC ^{34, 35, 38}, optical microscopy ^{35, 37} and depolarized-light intensity ³⁵. The maximum crystallization rates occur around 105°C ^{35, 38} and the overall crystallization rate increases with decreasing molecular weight ^{33, 35}. Regime II to regime III transition is often observed, although it appears at different temperatures such as 115°C ³⁸, 120°C ³⁷ or 140°C ³⁶. Vasanthakumrai and Pennings ³³, on the other hand, found that while high molecular weight PLLA only crystallized in regime II, low molecular weight PLLA exhibits a transition from regime II to regime I at 163°C, with corresponding morphology change from spherulitic to axialite. Avrami index as 3 ^{34, 38} and 4 ³⁵ were reported, however, with different origins: heterogeneous nucleation and three-dimensional growth ³⁸, homogeneous nucleation and two-dimensional linear growth ³⁴, or homogeneous nucleation and three-dimensional growth ³⁵ were all cited.

The degradation of PLAs can undergo thermal, hydrolytic or biological mechanisms. Although the reported equilibrium melting temperature is around 206°C-215°C ^{32, 33, 38, 39}, PLLAs processed in this temperature range would be anticipated to suffer severe molecular weight reduction according to independent studies by

Jamshidi et al.⁴⁰ and Bigg⁴¹, giving a very small window for PLLA processing. Improvement on the thermal stability can be achieved by removal of residue monomers and catalyst^{40, 41} or by end capping the chains⁴⁰. As for hydrolytic degradation of PLAs, initial degree of crystallinity greatly influences its rate because preferred hydrolysis takes place in disordered amorphous regions, followed by the highly organized crystalline regions, which leads to the final break down of the material.

2.2 COLD CRYSTALLIZATION AND DOUBLE COLD CRYSTALLIZATION

While cold-crystallization (T_cI) phenomena commonly occur in the DSC scans of amorphous or partially crystallized polymers when heated above the glass transition temperature, double cold-crystallization (T_cI and T_cI' , as in **Figure 2.4**) is not often seen. This phenomena has been reported previously in unoriented PET films⁴²⁻⁴⁴ as well as uniaxially oriented PET fibers⁴⁵, although never in PLLA. Zhu et al.⁴²⁻⁴⁴ suggested that T_cI and T_cI' reflect the crystallization from the interlamellar and interspherulitic amorphous regions, controlled by the extent of nucleation and diffusion. Interlamellar amorphous regions, which consist of chain folds, chain ends, and tie chains, have some order compared with completely amorphous interspherulitic regions so that they crystallize at lower temperature. When nucleation is dominant (high supercooling, crystallization from the glassy state), more interlamellar amorphous regions are formed than interspherulitic ones. On the other hand, when the diffusion is dominant (low supercooling, crystallization from the melt), more interspherulitic amorphous regions can be expected than interlamellar ones. Normal

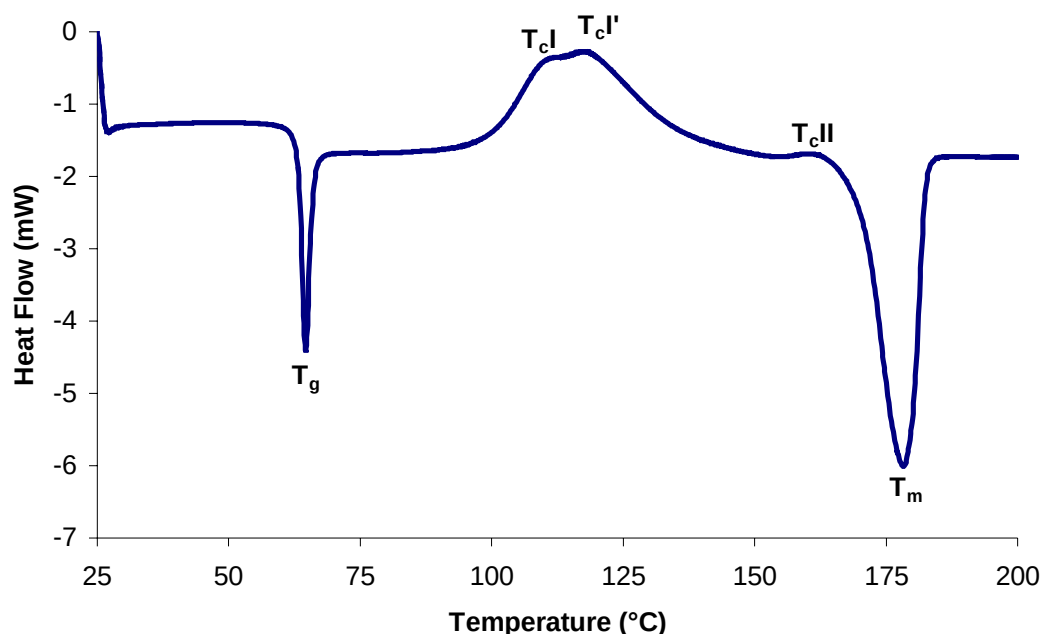


Figure 2.4 Typical DSC Curve of Amorphous PLLA Film, 10°C/min

DSC detected one T_g , while two T_g s appeared in some cases using DMA. Lu et al.⁴⁵ believed that the double melting is related to two crystallization processes (crystal growth dimensions) characterized by Avrami index 1 and 2, at lower and higher temperature accordingly. Another group⁴⁶ also proposed that the occurrence of double cold-crystallization is related to the humidity of storing place and the time of storing. Moisture causes the surface energy to drop, thus facilitates the crystallization, resulting in the lowering of the crystallization temperature.

2.3 MULTIPLE MELTING PEAK PHENOMENA IN POLYMERIC MATERIALS

2.3.1 Poly(ether ether ketone) – PEEK – a semi-flexible polymer

PEEK is a high-performance engineering plastic, especially as a matrix for fiber-reinforced composites. (**Figure 2.5**) It is reported to have only a single crystal

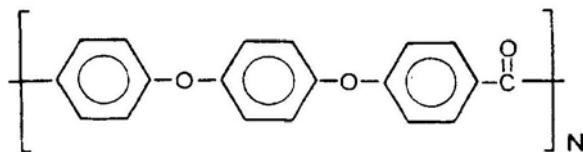


Figure 2.5 Chemical Structure of Poly(ether ether ketone) (PEEK)

form: orthorhombic ⁴⁷. The absence of polymorphic transition thus excludes the possibility of two different crystal structures that could be assigned to the dual melting peaks often observed in PEEK thermographs. It also has an extremely large temperature interval of crystallization ($T_g \sim 140^\circ\text{C}$, $T_m \sim 385^\circ\text{C}$), which provides plenty of room for the extensive research on its crystallization and melting behaviors.

Unlike the melting behavior of other polymers in the same class such as poly(ethylene terephthalate) (PET) ⁴⁸, poly(butylene terephthalate) ⁴⁹ and poly(phenylene sulfide) ⁵⁰ which usually display triple melting peaks when scanned in DSC, that of PEEK often exhibits only two melting peaks, T_{mI} being noted as low endotherm melting peak and T_{mII} as high endotherm melting peak. When three endotherms are observed (in polymer exhibiting a single-crystal phase), the lowest and middle melting peaks were attributed to the secondary and primary crystals, respectively, formed at the crystallization/annealing temperature prior to the scan. The lowest endotherm usually occurs just a few degrees above the original crystallization/annealing temperature. The third and highest melting endotherm was associated with the melting of more stable crystals that recrystallized from the middle endotherm during the scan ⁵¹. It seems the conflicting debate emerges when two endotherms are presented.

The two major hypotheses proposed to explain dual melting peaks observed in PEEK are: (1) the *melting-recrystallization* model⁵²⁻⁵⁹ and (2) the *dual lamellae population* model^{51, 60-74}. Considering the spatial distribution of these lamellae within PEEK spherulites, hypothesis (2) is further divided into two sub-models: lamellae insertion model^{51, 61, 63-69, 71, 73, 74} and lamellae stack model^{60, 62, 70, 72}. Nevertheless, in all cases, it is suggested that (1) the T_{mI} is about 10-20°C above the designated crystallization/annealing temperature, (2) x-ray experiments indicates only one crystal structure existed for either cold-crystallized (crystallize from the glassy state) or melt-crystallized (crystallize from the melt) PEEK, and (3) ΔH_{mI} increases and T_{mI} shifts to higher temperature with increasing crystallization/annealing temperature or time.

Blundell and Osborn⁵² first reported the occurrence of dual melting endotherm in PEEK. They believed that T_{mI} is the actual characteristic melting point of the majority of the crystals present in the DSC sample at room temperature prior to the heating scan. It is therefore associated with the melting of initial crystals formed during the previous isothermal crystallization. During the subsequent scan above T_{mI} , the polymer undergoes continuous melting and recrystallization processes when original crystals become unstable. T_{mI} thus accordingly marks the onset of where the melting and recrystallization occurs. The T_{mII} represents the point where the net difference of the ongoing competition between the melting and recrystallization passes through a maximum. It is the melting of the more perfect crystals or thicker lamellae developed through the heating scan.

Blundell⁵³ later reinforced his hypothesis by the partial melting of PEEK samples at three different temperatures between T_c and T_{mII} during a heating scan.

One would expect a continuous change as a result of the recrystallization process if hypothesis (1) is correct. Due to its systematic increase of crystal perfection during the heating scan, when the heating is interrupted, a crystal population of greater stability than the originals will be “remembered”. During the subsequent reheating, the melting and recrystallization process will theoretically recur and another corresponding T_{mI}' will appear at a higher temperature than where the scan was stopped. On the other hand, if hypothesis (2) is correct, no substantial change should be detected until T_{mII} is reached. The experiment results obtained are strongly in favor of hypothesis (1). In the same study, it was also found that the increasing of heating rate shifts the position of T_{mI} and T_{mII} in opposite direction, which is consistent with other groups’ observations^{54, 55, 57, 58}.

Lee *et al.*^{54, 55} spread their research on heating rate effect on not only the cold-crystallized samples (high supercooling), but also the melt-crystallized samples (low supercooling). A noticeable difference was observed in their melting behavior. For cold-crystallized PEEK samples (**Figure 2.6**), the heat of fusion and endotherm of T_{mI} increase with increasing heating rate, while those of T_{mII} decrease. It was proposed that, as the heating rate was increased, there was less time for recrystallization to take place, which results in a larger T_{mI} endotherm and a smaller T_{mII} endotherm. The size and perfection of the recrystallized PEEK decreases with increasing heating rate due to the shorter reorganization time, leading to the decrease in T_{mII} . In contrast, for melt-crystallized samples, T_{mII} does not change with heating rate (**Figure 2.7**). It was believed to be related to the crystalline morphology produced at different degree of supercooling (high vs. low). Due to slow crystallization, the chain conformations at

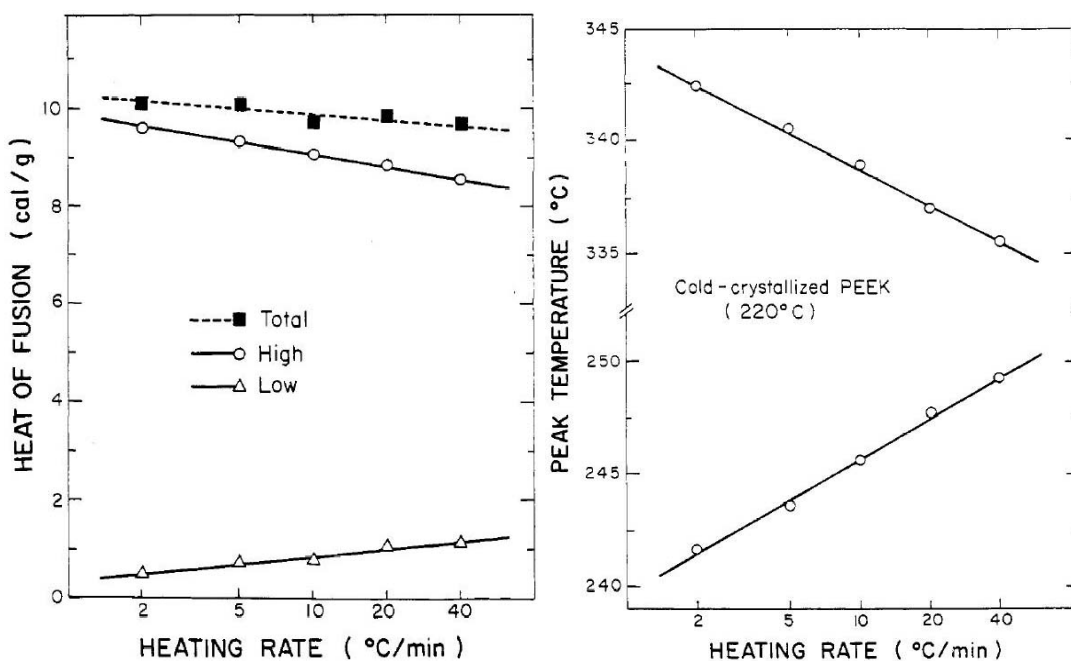


Figure 2.6 Heat of Fusion (left) and Melting Peak Temperatures (right) vs. Heating Rate.⁵⁴ (The PEEK samples were cold-crystallized at 220°C for 75 hrs.)

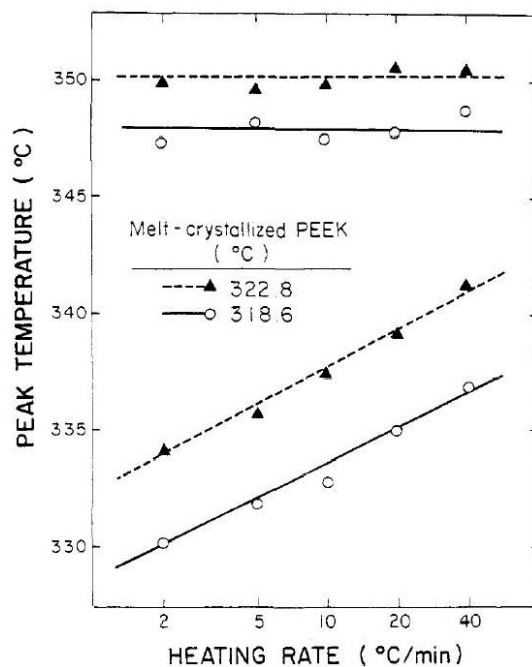


Figure 2.7 Melting Peak Temperatures vs. Heating Rate⁵⁴ (The PEEK samples were melt-crystallized at -▲-322.8°C for 20 hrs and -○- 318.6°C for 14 hrs.)

the crystal surfaces are more perfect in PEEK melt-crystallized at low supercooling than cold-crystallized ones. Consequently, the reorganization process of melt-crystallized samples is fast enough to be independent of heating rate changes. While Marand and coworkers⁷⁴ observed the similar trend, they are supporters of the *dual lamellae population* model. They seem to think that significant melting-recrystallization only exists in the primary crystals of cold-crystallized samples, while at most very minor reorganization took place during the heating of melt-crystallized samples, except possibly at very low heating rate as 5°C/min, because the location of T_{mII} is independent of heating rate.

Lee *et al.*^{54, 55} also proposed that T_{mI} represents only a portion of the melting endotherm of the original crystals and the double melting behavior can be explained as the sum of four contributions: melting of most original crystals, their recrystallization, remelting of crystallized PEEK, and melting of residual crystalline regions. A model, adapted from Rim and Runt's deduction from poly(ϵ -caprolactone)⁷⁵, was modified to interpret the dual melting endotherm of PEEK. According to the model, the area of the recrystallization exotherm equals that of the melting endotherm of the recrystallized material. As demonstrated in **Figure 2.8**, at a low heating rate, there will be a large recrystallization exotherm under the melting endotherm of original crystals and another melting endotherm of the recrystallized materials (remelting peak) at a higher temperature. The T_{mI} endotherm is determined as the sum of the recrystallization exotherm and the melting endotherm of the original crystals. As a matter of fact, true melting temperature can be obscured by continuous melting and recrystallization when reorganization is allowed. When the heating rate is increased,

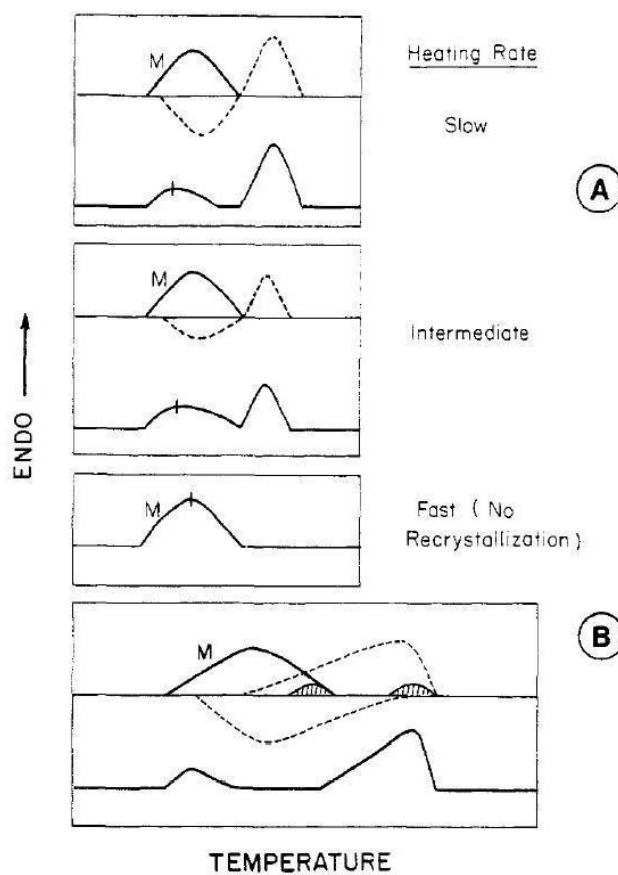


Figure 2.8 Schematic Representation of the Melting Mechanism Proposed for (A) Poly(ϵ -caprolactone), Adapted from Rim and Runt⁷⁵ and (B) PEEK (M represents the melting endotherm of the original crystals; the dotted lines represent the recrystallization exotherm and the melting endotherm of the recrystallized crystals; the shaded area in B represents melting of the core crystalline region)⁵⁴

the crystals will have less time to reorganize. The corresponding recrystallization exotherm as well as the remelting endotherm will both decrease in magnitude. At an even higher heating rate where recrystallization is restricted, the melting of only original crystals will be observed. Such a single endotherm represents the complete melting without reorganization of the original crystals. Meanwhile, the effect of thermal conductivity of polymer will become considerable as the heating rate increases so that superheating phenomenon will occur. As a result, they concluded that single melting endotherm, without being superheated, represent the true melting of original PEEK crystals that existed in the sample prior to the DSC heating scan. They also suggested that the reorganization process is considered to occur at crystal surfaces through partial melting followed by recrystallization. The melting of the core took place in the much later stage, as shown in **Figure 2.8 (B)**. Furthermore, it was claimed that no evidence for the existence of dual lamellar structures in both cold- and melt-crystallized polymer was found with SAXS⁵⁵. (**Figure 2.9**)

The exothermic recrystallization (portrait in **Figure 2.8**) could not be detected by conventional DSC due to the fact that the extent of exothermic recrystallization is less than that of endothermic melting. However, this limitation was overcome by Wei et al.⁷⁶ using Temperature modulated differential scanning calorimetry (TMDSC). As shown in **Figure 2.10**, the non-reversing (NR) curves exhibit strong exothermic behavior. The higher the crystallization temperature, the smaller the exothermic amount becomes. At 320°C (**Figure 2.10(B)**), the exothermic phenomenon is no longer detectable. They hence concluded that at crystallization temperature above 320°C, the *dual lamellae population* model is the sole mechanism of double melting

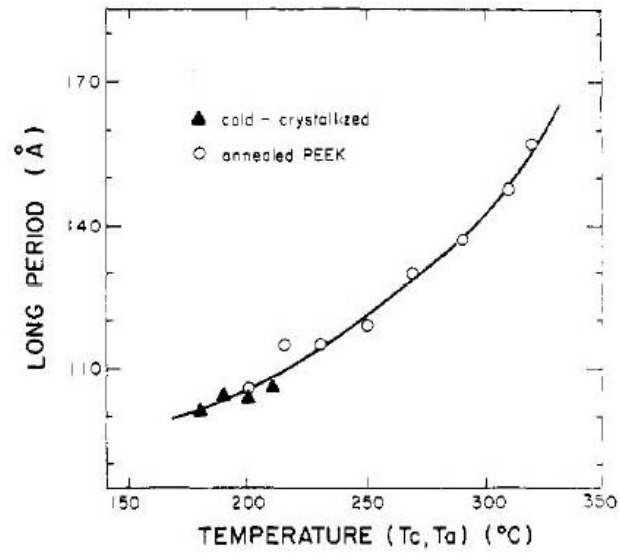


Figure 2.9 Long Period versus Crystallization Temperature for Cold-crystallized and Annealed PEEK ⁵⁵

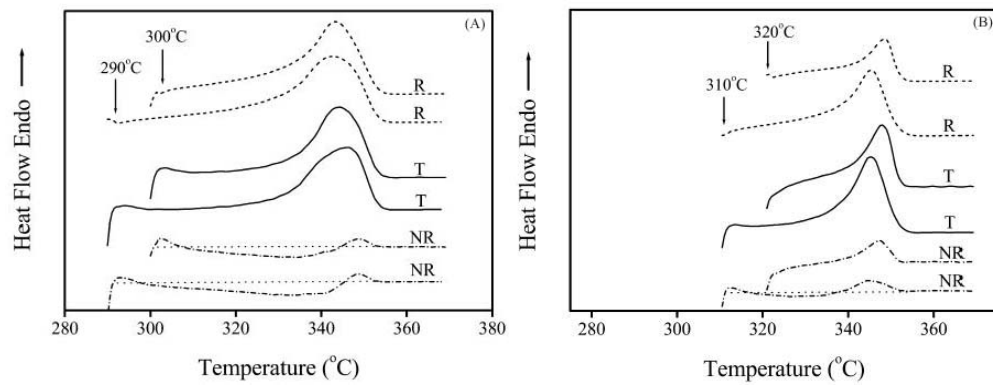


Figure 2.10 TMDSC Thermograms of Isothermally Melt-crystallized PEEK at (A) 290°C and 300°C, (B) 310°C and 320°C for 10 minutes ⁷⁶

peak phenomenon. On the other hand, below 320°C, they established a combined mechanism of hypothesis (1) and (2), i.e. T_mI endotherm is the superposition of early melting of secondary crystals with almost simultaneous recrystallization, and T_mII endotherm is the sum of perfected crystals from reorganization and the primary crystals. This conclusion is in agreement with Cheng et al.⁷⁷ and Chen and Woo⁶⁹.

Combining DSC with time-resolved SAXS and WAXS techniques, Fournies et al.^{57, 58, 78} were able to support the *melt-recrystallization* mechanism of a single population of crystals using cold-crystallized PEEK samples. However, they also found that^{57, 58, 78} high annealing temperature, around 340°C⁵⁸, yields samples in which two distributions of crystals coexist. The thicker one grows first during the isothermal crystallization while the thinner one forms during subsequent cooling non-isothermally (at -10°C/min). On the other hand, when the samples are prepared at lower temperatures, there exists no significant crystallization during the cooling phase and the resulting samples contain only lamellae crystallized during the isothermal crystallization. The analysis of correlation function of the SAXS data strongly supports their conclusions. The influence of heating rate on the peak positions are opposite in these two ranges, as shown in **Figure 2.11**.

Cebe and Hong⁷⁹, Cheng et al.⁷⁷ and Bassett et al.⁸⁰ were the first groups that support the hypothesis of *dual lamellar population* (or morphology) formed in two stages of crystallization, while Lattimer et al.⁶⁰ suggested that the two different lamellar populations have grown simultaneously. They all observed similar tendency in PEEK as Blundell⁵³ did, such as the increasing crystallization temperature and heating rate effects, for both cold- and melt-crystallized samples. Though many

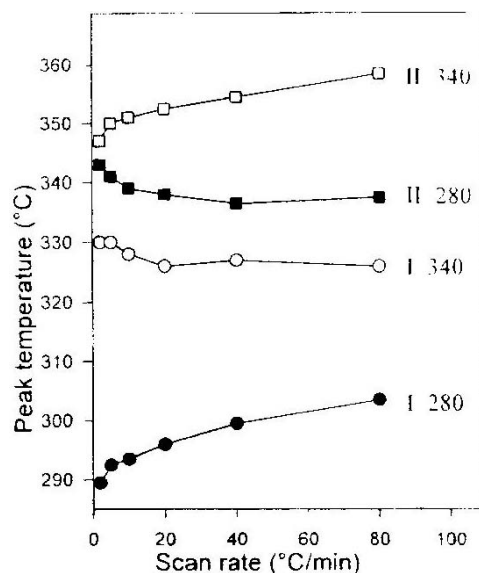


Figure 2.11 Peak Temperatures of T_{mI} (○,●) and T_{mII} (□,■) versus Heating Rate for Samples Prepared at 280°C (filled symbols) and 340°C (open symbols)⁵⁸

authors acknowledged the existence of possible reorganization during the heating scan, they were not convinced that *melt-recrystallization* cause the origin of the dual melting peak. While Cheng et al.⁷⁷ saw signs of T_{mI} reorganization to some degree, Bassett et al.⁸⁰ believed that no more than a modest extent of recrystallization (lamellae thickening) developed within T_{mII} itself at slower heating rate, which is agreed by Hsiao and coworkers⁶⁴. Cebe⁵¹ believed that such reorganization within T_{mII} led to the constant melting temperature regardless of treatment temperature. Cebe and Hong⁷⁹ chose 20°C/min as heating rate to minimize the reorganization, but found out that it was still not fast enough to prevent the crystals from reorganization into more perfect crystals during the heating scan. However, even at heating rate of 80°C/min, double melting peak feature is still prominent⁸⁰ as shown in **Figure 2.12(A)**. They thought reorganization should be suppressed by such a high heating rate because the crystallization rate above 300°C is relatively slow. Consequently,

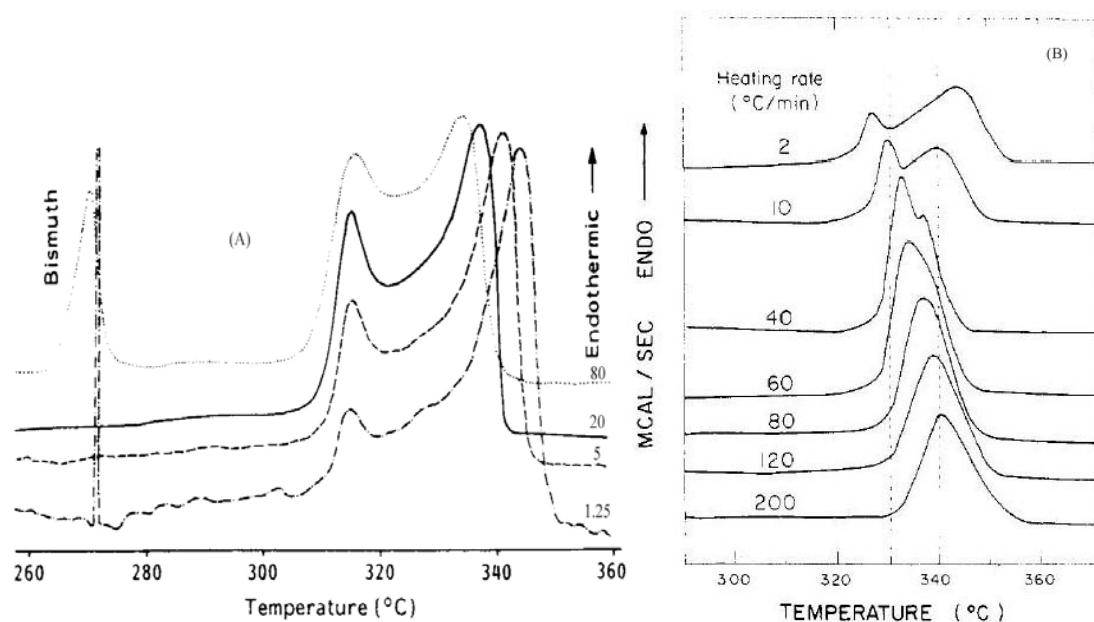


Figure 2.12 Heating Rate Effect of PEEK (A) Melt-crystallized at 310°C for 1h⁸⁰ and (B) Annealed at 320°C for 1h⁵⁵

they believed that the two endotherms were related primarily to the different initial crystal structures. However, for a sample with similar Mw, Lee et al.⁵⁵ found two endotherms at 40°C/min, but not at 60°C/min, and determined 60°C/min as the point where reorganization was diminished (**Figure 2.12(B)**). Their sample was annealed at 320°C for 1 hr and Bassett et al.'s⁸⁰ melt-crystallized at 310°C for 1 hr. Since the crystallization rate should be relatively faster at 310°C than 320°C, it is theoretically still feasible to see two peaks at 80°C/min. Also at 320°C the two peaks were closer to each other to start with, it could become one at a lower heating rate. Bassett et al.⁸⁰ substantiate hypothesis (2) by a simple direct test illustrated in **Figure 2.13** (very similar results reported by Cheng et al.⁷⁷ as well). Same specimens were melt-crystallized at 310°C for various times. It was clear that crystallites firstly formed

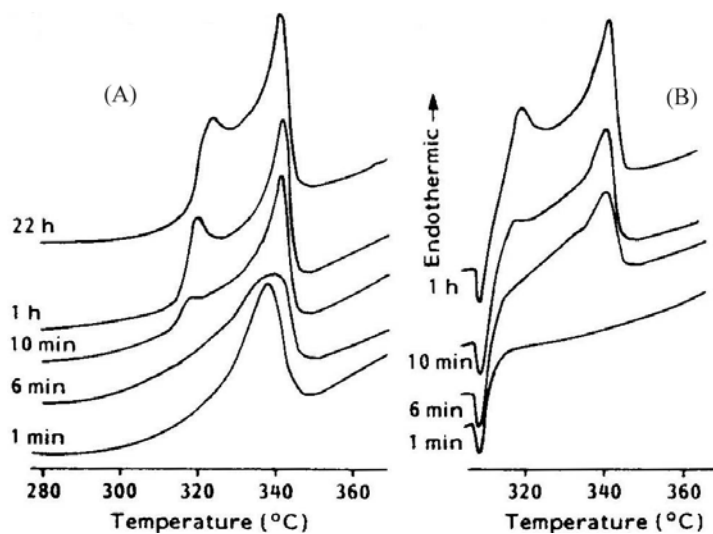


Figure 2.13 PEEK Melt-crystallized from 310°C for Different Time. (A) Cooled to 200°C and Rescanned; (B) Scanned Directly from the Crystallization Temperature⁸⁰

yield higher melting than those formed subsequently. Thus, T_{mII} cannot be formed from T_{mI} . Therefore, the two melting peaks represent two different components of the morphology (primary vs. secondary), which is backed by their electron microscopy (permanganic etching) results. The dominant primary crystallization was followed by infilling growth of secondary crystallization. Similar TEM observations were shown by other authors as well^{71, 73, 81}. With time, the ratio of T_{mI} and T_{mII} increases, and both peaks move to slightly higher melting temperature as crystallization proceeds⁷⁷. However, Blundell⁵³ had different explanation for such observation of **Figure 2.13**. At the early stages, just after crystallization has started, the crystals are less stable and the recrystallization occurs immediately after the heating scan starts, giving only T_{mII} observable.

Many groups pointed out the crystallization during cooling as another part of the contribution to the heat of fusion. When the crystallization temperature is sufficiently high, some material will not be able to completely crystallize in the time available, but will do so on subsequent cooling. The higher the temperature, the more contribution derived from the cooling. It appears to be a broad melting endotherm below the crystallization/annealing temperature, just as pointed out by Fournies and coworkers^{57, 58, 78}. However, Cheng et al.⁷⁷ suggest T_{mI} and T_{mII} endotherms as two different morphology generated prior to the heating scan and crystallization during cooling, T_{mc} endotherm, being a third kind. They had the same sample scanned with and without cooling (at $-0.31^{\circ}\text{C}/\text{min}$) before analysis. Their results confirmed the contribution of the crystallization during the cooling, especially at higher crystallization temperatures, is significant. In **Figure 2.13**, the distinctive contribution of cooling is shown at 1 min crystallization.

Cebe and Hong's⁷⁹ results also do not support the assignment of the high temperature endotherm T_{mII} to crystals formed solely during the DSC scan (through *melt-recrystallization*). They pointed out that the volume fraction of crystals was about 25-30% in the temperature range studied by Blundell and Osborn⁵². As the area under T_{mI} endotherm was too small (2-4%) to account for melting of this crystal fraction, fairly good agreement was obtained with the crystal fraction determined from T_{mII} endotherm. Hence, they gave an alternative explanation that in such a temperature range of rapid crystallization investigated, secondary crystallization may have occurred through the formation of small, imperfect crystals between existing lamellae, giving rise to the small endothermic response at low temperature. However,

they may fail to take into consideration the fact that T_{mI} endotherm is actually the sum of the recrystallization exotherm and the melting endotherm of the original crystals, as clearly demonstrated by Lee et al.⁵⁴ in **Figure 2.8**.

Hsiao et al.⁶⁴ based their conclusion of *dual lamellae population* model on time-resolved SAXS. They noticed that long period derived from both Bragg's Law (L_B) and correlation function (L_C^M) indicates two stages of increase at a transition temperature near T_{mI} (**Figure 2.14**). Before the melting of any crystallite, a relatively small thermal expansion of both the crystalline and amorphous components causes slight increase of the long period. At temperature above T_{mI} , these thinner lamellae will be melted away, leaving only the thicker lamellae in the stacks, as illustrated in **Figure 2.15**. Consequently, the mean long period will increase gradually at the second stage of larger increase.

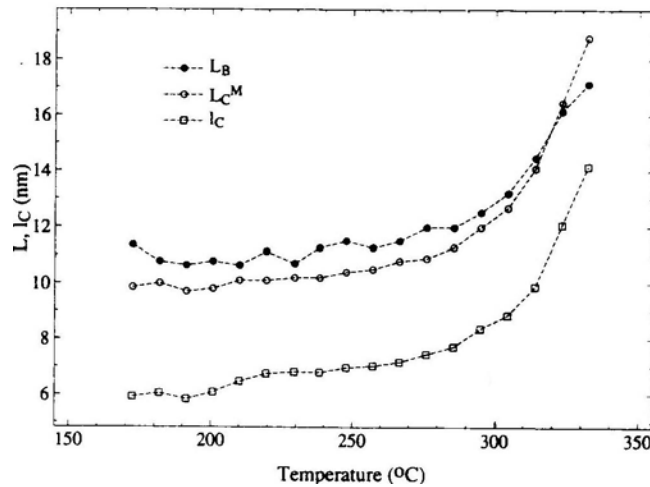


Figure 2.14 Two Types of Long Period (L_B and L_C^M) and Lamellar Thickness versus Temperature⁶⁴

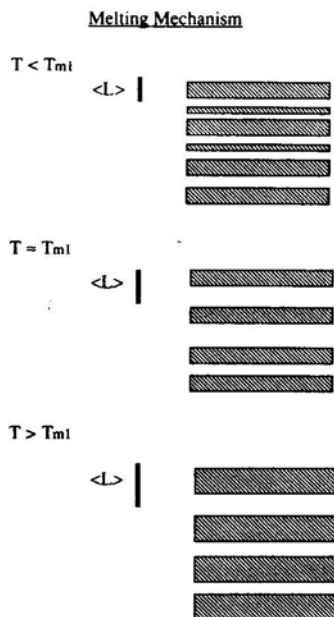


Figure 2.15 Schematic Representation of the Melting Mechanism for the Dual Lamellar Thickness Model (the thinner shaded bars represent the secondary lamellae and the thicker ones represent the primary lamellae which are subsequently thickened) ⁶⁴

Also using time-resolved SAXS plus the combination of correlation function and interface distribution function analysis, Verma et al. ⁷² used the lamellar stacks model rather than lamellae insertion model to interpret the dual melting behavior of PEEK, which is consistent with TEM observations by Lattimer et al. ⁶⁰. Their results indicate that the long period and the lamellar thickness rise during melting, and the amorphous layer thickness decreases upon heating through T_{mI} , while for lamellar insertion model to be accountable, all three parameters should be expected to increase.

2.3.2 Other semi-flexible polymer

Other semi-flexible polymers that normally exhibit multiple melting peaks include, but are not limited to, isotactic polystyrene (iPS) ⁸²⁻⁸⁷, Poly(ethylene

terephthalate) (PET)^{48, 81, 88-93}, and poly(butylene terephthalate) (PBT)^{49, 94, 95}. Dual^{49, 81, 82, 88-90, 92, 94, 95} as well as triple melting peaks^{48, 49, 83-87, 91, 93} were observed depending on the thermal history experienced.

As mentioned earlier, the widely accepted assignment for triple melting peaks is secondary, primary, recrystallized primary crystals (T_a , T_{mI} , T_m T_{mII}) respectively. Such mechanism was confirmed by Lemstra and coworkers^{83, 84} for melt-crystallized iPS, by Ahmad and Al Raheil⁴⁸, Zhou and Clough⁹¹ for PET, and by Kim and Robertson⁴⁹ for PBT.

Nevertheless, other possible mechanisms were carefully proposed to explain the appearance of triple melting peaks. Combining conventional DSC with TMDSC and TEM, Liu and coworkers^{85, 86} concluded that, for cold-crystallized iPS, T_a was not originated from the melting of the secondary crystals, but associated with a constrained interphase between the amorphous and crystalline phase going through a enthalpic relaxation process during DSC heating. Though T_{mI} and T_{mII} were assigned to two kinds of lamellar components of different thermal stability, they did not rule out the partial contribution of recrystallization to T_{mII} .

Based on the results of polarized optical microscopy (POM), DSC, WAXD and SAXS, Medellin-Rodríguez et al.⁹³ proposed another alternative mechanism. They believed that both T_a and T_{mI} originate from secondary crystallization, with the former generated at the last steps, and T_{mII} stems from primary melt-crystallization, accompanying with some extent of recrystallization within its development.

As for the case of dual melting peaks, Bell and Murayama⁸⁸ characterized them as folded chain versus partially extended chain crystals, while Roberts⁸⁹

suggested bundle-like versus chain folded crystals. However, both propositions seemed to neglect the effect of thermal scanning. Although, Kim and Robertson⁴⁹ observed triple melting peak behavior of PBT at long melt-crystallization periods, only two peaks were revealed at shorter crystallization time. The origin of these two peaks was credited to the *melt-recrystallization* model. Qudah and Al Raheil⁹² came to the same conclusion for PET with the evidence from SEM, which showed the existence of only one type of lamella within the spherulite. Moreover, this exact model was also supported in iPS⁸², PET^{81, 90} and PBT⁹⁵ systems by different research groups.

2.3.3 Polypropylene – PP – a flexible polymer

PP is a simple, flexible, widely used polymer that has an apparent melting point similar to PLA. The origin of its multiple melting peak is, however, very complex. Either one or two melting peaks were reported in the literature depending on the thermal history. The melting of PP is affected by many factors, such as molecular weight, molecular weight distribution, degree of tacticity, head-to-tail sequences, and the presence of different crystal forms. Isotactic PP (iPP) will be the focus in this section instead of syndiotactic PP (sPP). iPP is a polymorphic material with the tendency to crystallize into different crystal modifications such as monoclinic (α), hexagonal (β), and triclinic or orthorhombic (γ). The α -crystal is most frequently formed during the crystallization of industrial iPP grades, while the β -crystal can also appear at higher supercooling. The γ -crystal is often observed in degraded, low MW

PP or when it crystallizes under high pressure. It is also found in iPP containing small quantities of a comonomer.

Due to its polymorphic characteristics, a third mechanism, *dual crystal structure model*, was attempted to interpret the multiple melting behavior of iPP. As shown in the optical micrographs in **Figure 2.16**, the light transmission measurements showed that, samples isothermally melt-crystallized below 132°C, the tail T_{mI} endotherm is due to the melting of β -spherulites and the broad T_{mII} endotherm is due to the melting of crosshatched and radiating lamellae in α -spherulites. On the other hand, although double melting endotherms still appear above 132°C, only α -spherulites were formed. Al-Raheil et al.⁹⁶ assigned T_{mI} as the melting of crosshatched lamellae in α -spherulites, while T_{mII} as the melting of the radial and the reorganized tangential lamellae.

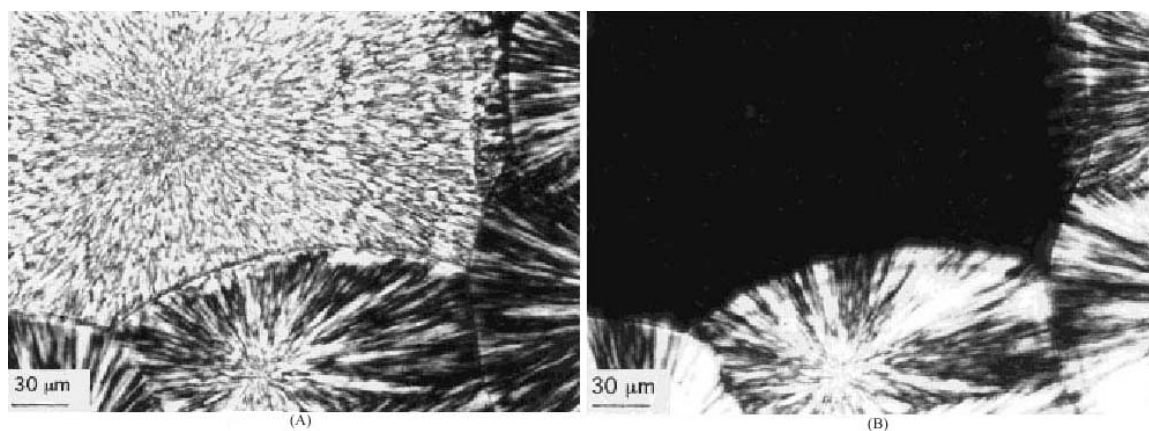


Figure 2.16 Optical Micrographs of iPP Samples Isothermally Melt-crystallized at 128°C. (A) Showing α - and β -spherulites and (B) Showing Separate Melting of β -spherulites⁹⁶

Co-existence of α - and β -crystals also arose in the melt-crystallized iPP thick plates molded by intrusion ⁹⁷. A variable proportion of the α - and β -crystals developed over the thickness of the plates, ranging from 0% of β -crystals at the surface to 60vol% at the core. DSC thermograms (**Figure 2.17(right)**) showed double melting endotherms at 155°C and 170°C from the core material and only one peak from the surface material. Parallel examinations of the SEM and X-ray patterns (**Figure 2.17(left, middle)**) further confirmed unambiguously Aboulfaraj et al.'s ⁹⁷ postulation that the two peaks represent the melting of the β - and α -crystals, respectively. Quite different contrasts were observed in SEM due to the nature of lamellae structure of each modification. For the α -spherulites, lamellae are straight and interlocked in a crosshatched array of the radial and tangential direction and the corresponding etched sections are very smooth. In contrast, the β -spherulites are characterized as curved and twisted lamellae, making the etched surface rougher. Consequently, more secondary electrons emitted from rougher surface to the detector, resulting in dark α -spherulites and much brighter β -spherulites.

Based on the results above, it seems quite possible to have only α -crystal observed for thin film samples usually used by other groups. Among them, De Rosa and coworkers ⁹⁸⁻¹⁰¹ not only claimed that the double endotherms were due to the *melt-recrystallization* mechanism, but also proposed such a process occurred over the “continuum” transitions from a disordered limiting structure (α_1) having crystallographic symmetry $C2/C$ to a ordered limiting structure (α_2) having crystallographic symmetry $P2_1/C$. These two limiting structures of the α -crystal show

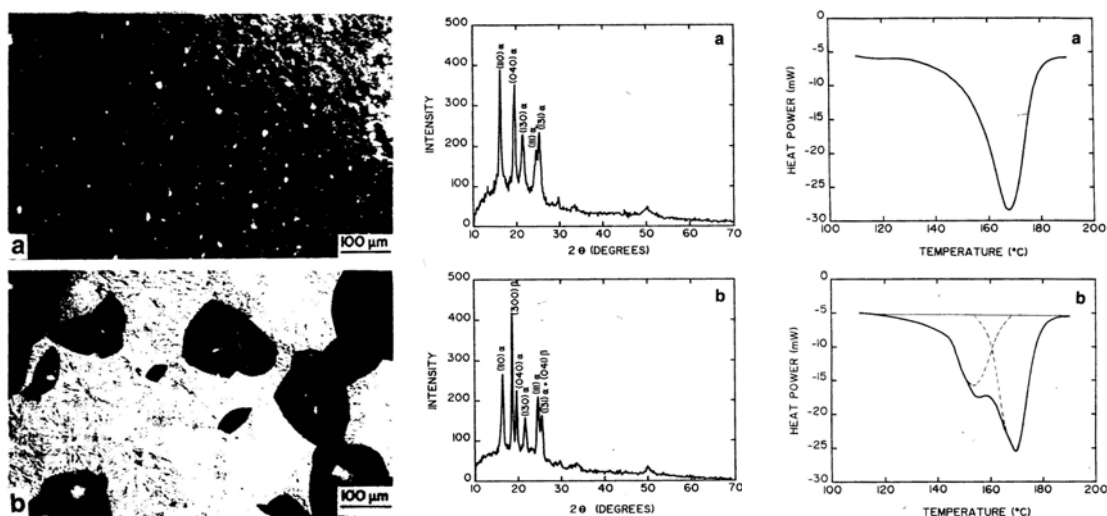


Figure 2.17 Scanning Electron Micrographs (left), X-ray Diffraction Patterns (middle) and DSC Thermograms (right) of iPP Plate Obtained for Samples Taken from (a) the Surface Region; (b) the Core Region⁹⁷

various degrees of disorder in the up and down positioning of the chain with α_2 -crystal having a lower free energy than the α_1 -crystal. Although they have substantially identical X-ray spectra, only reflections with $(h+k)$ even are allowed in the α_1 -crystal, while $(h+k)$ uneven reflections may be present in the α_2 -crystal with a lower intensity in general. Based on this, the ratio of α_1 vs. α_2 crystal was easily evaluated.

In order to clarify any doubt about the origin of double melting endotherms, nitric acid etching experiments were performed by Petraccone et al.¹⁰² on samples melt-crystallized at 135-150°C. Since the etching treatments remove the amorphous portions of the macromolecules as well as the folds at the crystal surfaces, the reorganization should necessarily be hindered. **Figure 2.18** illustrates the melting endotherms of the sample crystallized at 148°C, before and after the etching. Only one narrow peak was seen in **Figure 2.18(B)**, which substantiates the *melt-*

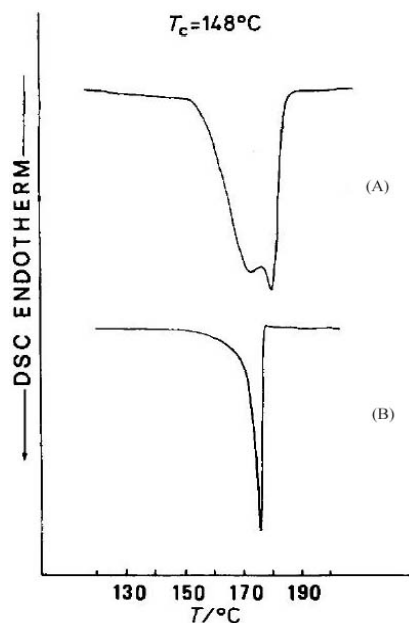


Figure 2.18 DSC Melting Scans at 10°C/min for iPP Sample that (A) Crystallized at 148°C and (B) Crystallized at 148°C and Subsequently Subjected to the Etching Procedure¹⁰²

recrystallization mechanism towards the appearance of double melting endotherms. In addition, such a peak should correspond to the true melting of the unique species crystallized at T_c .

While some groups were convinced by *melt-recrystallization* model, others^{103, 104} favor the *dual lamellae population* model. For iPP of low degree of stereoregularity, Martuscelli et al.¹⁰³ attributed T_{mII} and T_{mI} to crystals grown during the primary and interfibrillar secondary crystallization process, respectively. By partially melting a specimen between the two peaks, Weng et al.¹⁰⁴ assigned T_{mII} to radial dominant lamellae and T_{mI} to mostly tangential subsidiary lamellae filling the space in between the dominants. Meanwhile, still others¹⁰⁵⁻¹⁰⁸ suggested the combination of both models emerging at different temperature ranges.

Yadav and Jain ¹⁰⁵ supported *melt-recrystallization* mechanism for samples melt-crystallized under 133°C. As shown in **Figure 2.19**, only a single melting peak was observed at either lowest or highest heating rates. When the heating rate was extremely low, almost all crystals underwent recrystallization and only T_{mII} was present, similar to the case of PEEK that experienced very short crystallization time ⁸⁰. As mentioned before, when heating rate increases, not enough time was available for recrystallization, then only T_{mI} was disclosed. Since the reorganization or recrystallization decreases with T_c , above certain temperature, in this case 133°C, the presence of crystalline species having different degrees of crystal disorder become the reason behind double melting peak.

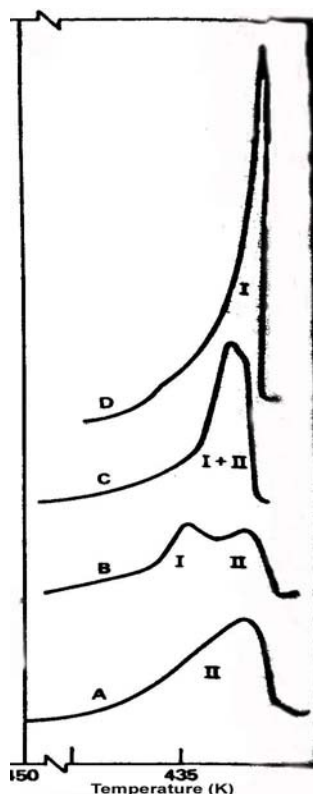


Figure 2.19 DSC Thermogram for Melt-crystallized iPP at 111°C, Effect of Heating Rate, Curve A, B, C, and D are for Heating Rate of 2,4,8,16°C/min ¹⁰⁵

Janimak et al.¹⁰⁶ separated two mechanisms by the degree of supercooling using DSC and time-resolved SAXS techniques. When the supercooling is $> 48^{\circ}\text{C}$, only poor and imperfect crystals could have formed, *melt-recrystallization* model dominants. For supercooling $< 48^{\circ}\text{C}$, two different crystal morphologies were recognized with different thermal stabilities and crystallization kinetics.

Last but not least, Zhu et al.¹⁰⁸ also detected *melt-recrystallization* for samples melt-crystallized at $T_c < 117^{\circ}\text{C}$, whereas *dual lamellae population* developed for those crystallized above 136°C . However, in the intermediate temperature range, the lamellae formed were affirmed to be perfect so that only a single peak of a single distribution of lamellar thickness was shown with the observation of DSC, WAXD and SAXS.

Finally, because of the enormous market of iPP, lots of various grades are available to different research groups, which make it extremely difficult to compare the experimental results and generalize common conclusions. The same case applied to sPP¹⁰⁹⁻¹¹⁴, which will not be discussed here.

In summary, it seems that different crystallization and melting events may occur in different polymers, due to the difference in segmental mobility, chain conformational defects and diffusive processes.

2.3.4 Dual melting behavior of PLA

Double melting behavior has also been observed in PLLAs. Fischer et al.¹¹⁵ observed two distinctive melting peaks of undegraded solution-grown single crystals of PLA. However, no detailed interpretation or even DSC thermograms were given.

Jamshidi et al.⁴⁰ found that polymers with molecular weights lower than 3000 exhibit weak and broad endotherms at temperatures slightly lower than the main peaks. They suggested that those broad peaks be attributed to the unstable crystallized region and disappears with increasing molecular weight. Again they did not perform further investigations. Migliaresi et al.¹¹⁶ saw possible double melting behavior (**Figure 2.20**), i.e. a small exotherm just before the major melting endotherm peak in compression-molded PLLA, while no proper argument was presented. They¹¹⁷ also observed double melting in PLLA with low molecular weight (18,000), and an exothermic peak just prior to melting in PLLAs with higher molecular weights. Iannace and Nicolais³⁸ observed the same behavior for PLLA crystallized under 105°C, which they attributed to as the “cold crystallization”. In addition, double endothermic peaks were often detected in PLLA fiber form^{17, 118-121}. It was suggested that the occurrence depends largely on the initial melt-spinning and subsequent drawing conditions, but no further results are reported. However, this is out of the scope of this research, which deals with PLLA amorphous films. Yasuniwa et al.¹²² and Ohtani et al.¹²³ reported at approximately the same time their investigations in regard to the double-melting of PLLAs, but from different perspectives. Yasuniwa et al.¹²² believe that the absence of double melting in PLLA is definitely expected due to the mismatch of usual experimental conditions. According to their CR-HR map (**Figure 2.21**) for PLLA sample with $M_w=3\times10^5$ ¹²², it is clear that only under certain combination of the cooling rate (of dynamic non-isothermal crystallization) and subsequent heating rate, will double melting peak emerge. However, their research is limited only to non-isothermal melt-crystallization. Ohtani et al.¹²³ attempted to

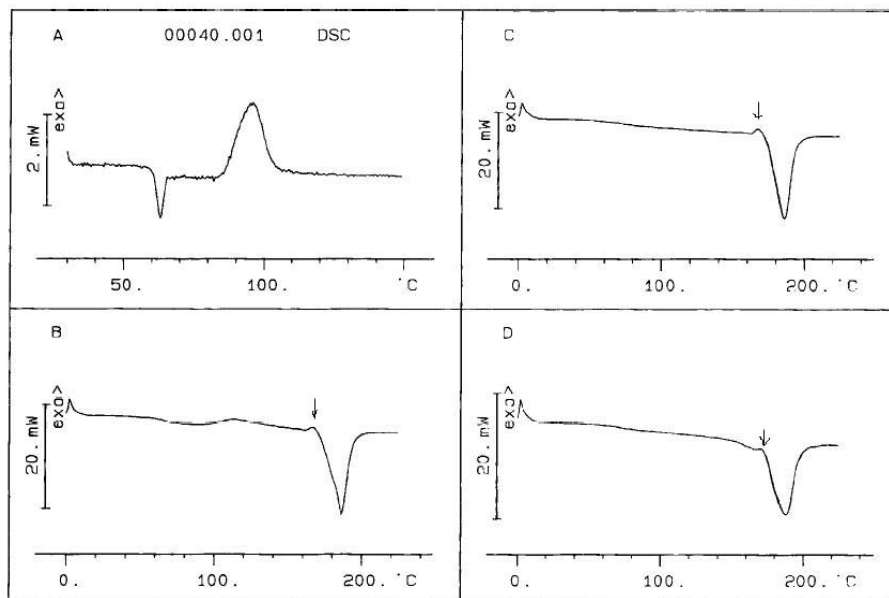


Figure 2.20 DSC Thermograms for (A) Amorphous PLA40 and Samples Treated in the DSC up to (B) 95°C, (C) 110°C, and (D) 150°C ¹¹⁶

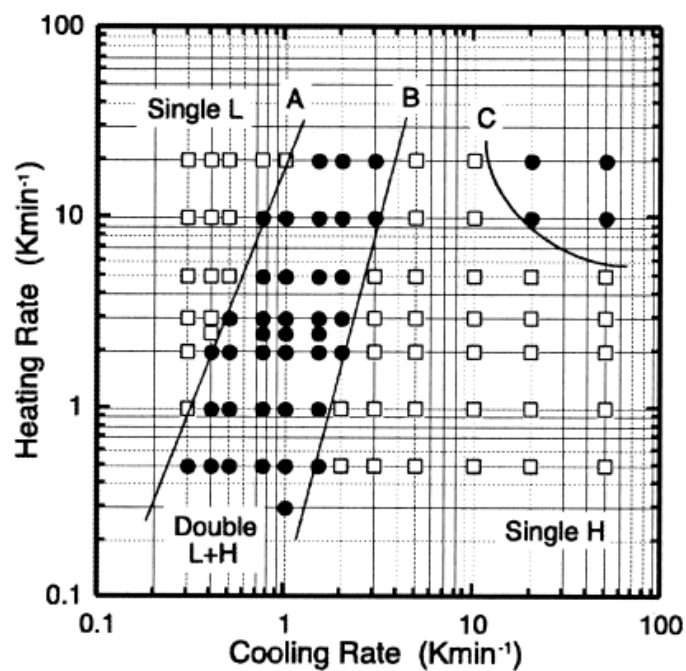


Figure 2.21 CR-HR Map of the Appearance of Double Melting Peaks of PLLA (-●- double melting peaks and -□- single melting peak) ¹²²

explain the structural origin of the extra exotherm also observed by others¹¹⁶ by studying isothermal cold crystallization of amorphous PLLA samples. They noticed a discontinuity in the melting temperature for samples cold crystallized at different temperatures, which is at 120°C. According to their analysis of WAXD patterns (**Figure 2.22**), they speculated from the absence of (011) and (103) reflections for samples treated below 120°C that β -crystal formed, while α -crystal grew only for samples treated above 120°C. It is, however, rather questionable whether a β -crystal grows from the fast quenched amorphous sample, when there are no such indication so far in the literature other than drawing induced β -crystal^{16, 17}. In contrast, Yasuniwa

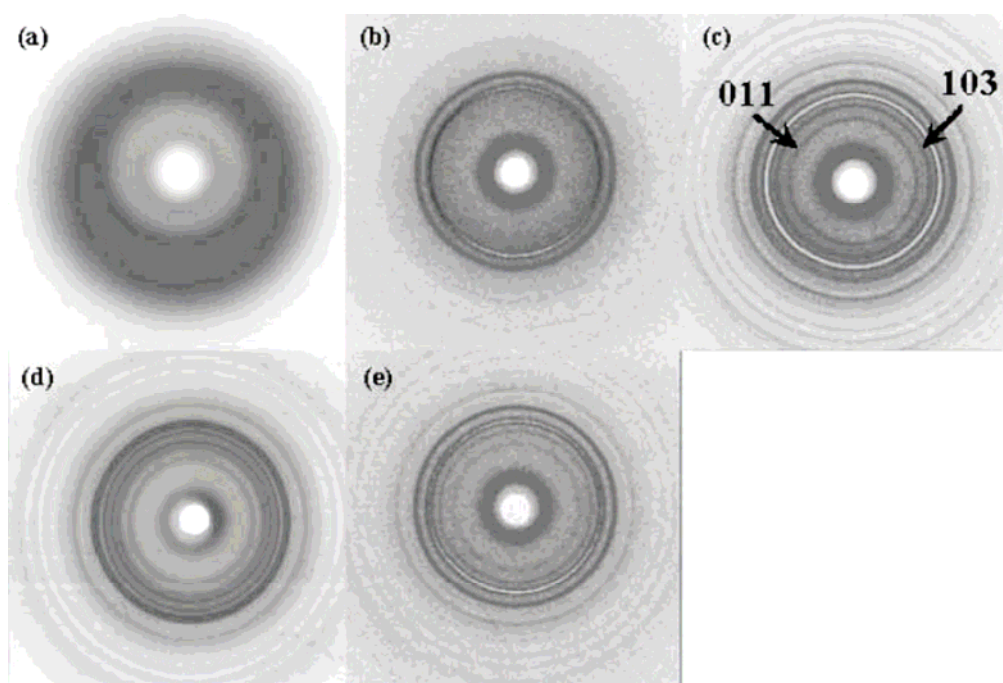


Figure 2.22 Wide-angle X-ray Diffraction Patterns of Various Samples: (a) As-prepared, Amorphous PLLA, (b) By One-step Annealing at 90°C for 20 min, (c) By One-step Annealing at 160°C for 1 h, (d) By Two-step Annealing (the first step at 90°C for 20 min, and the second step at 160°C for 10 min), and (e) Melt-crystallized by Ambient Cooling from Melt at 200°C¹²³

¹²² and Fisher ¹¹⁵ both agreed that the double melting of PLLA stems from melt-recrystallization. Consequently, part of the objectives of this research is to try to establish a clearer view of the double melting peak behavior of bulk PLLA in terms of different process conditions.

2.4 EQUILIBRIUM HEAT OF FUSION, $\Delta H_m(T_m^0)$ AND MELTING TEMPERATURE, T_m^0

2.4.1 Equilibrium heat of fusion, $\Delta H_m(T_m^0)$

Since polymers are normally semicrystalline, indirect methods must be used to evaluate the equilibrium heat of fusion of the crystal. It can often be achieved by conventional extrapolation from the calorimetric measurement of heat of fusion as a function of the degree of crystallinity (or specific volume) derived from an independent measurement. This method requires the knowledge of the specific volume of a perfect crystal, and a reasonably drawn baseline.

Another method involves the melting point depression developed on the thermodynamic of melting in polymers by Flory and coworkers ¹²⁴⁻¹²⁶, as expressed in the general equation:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_m} \ln X_A \quad (2.1)$$

$$X_A + X_B = 1 \quad (2.2)$$

where X_A is the mole fraction of crystallizable polymer, X_B is the mole fraction of impurity, R is the gas constant, and ΔH_m is the heat of fusion per mole of crystalline mer. ¹²⁷. For small value of X_B :

$$-\ln X_A = -\ln(1-X_B) \cong X_B \quad (2.3)$$

When the polymer chain end mers are considered a special type of impurity due to their different chemical structure from the mers along the chain, the above equation turns into:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = \frac{R}{\Delta H_m} \frac{2M_o}{M_n} \quad (2.4)$$

where M_o is the molecular weight of two identical end mers, and M_n is the number average molecular weight, thus $2M_o/M_n$ gives the mole fraction of the chain ends. It seems that the melting point depends on the molecular weight and the equation predicts the highest possible melting temperature occurs at infinite molecular weight.

In the case of mixing with a diluent (solvent, random copolymer unit or plasticizer), it is slightly more complicated:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = \frac{R}{\Delta H_m} \frac{V_u}{V_1} (\nu_1) \quad (2.5)$$

where V_1 is the molar volume of the solvent, V_u is the molar volume of the polymer repeat unit, and ν_1 is the volume fraction of the diluent. Further taken into consideration of the interaction between the polymer and the solvent, it becomes the well-known Flory-Huggins equation:

$$\frac{1}{T_m} - \frac{1}{T_m^\infty} = \frac{Rx'}{\Delta H_m} \left[(1-\nu_2) - \chi(1-\nu_2)^2 \right] \quad (2.6)$$

where T_m is the apparent melting temperature, ΔH_m is the heat of fusion per repeating unit, x' is the ratio of partial molar volumes of the polymer repeating unit to the diluent, χ is the interaction parameter, and ν_2 is the volume fraction of the polymer.

ΔH_m can be determined from the slope of $\left(\frac{1}{T_m} - \frac{1}{T_m^\infty} \right) / (1 - v_2)$ versus $(1 - v_2)$. The advantage of the diluent methods is its independence of the measurement of crystallinity, while it encounters major difficulties such as possible phase separation and the requirement of same lamellar size and crystal perfection at T_m ¹²⁸. In an extensive study of iPP, Isasi et al.¹²⁹ implied that the melting point depression by low molecular weight diluents is the most reliable way of obtaining ΔH_m° for a polymer.

These two basic methods can give widely varying results mainly due to the experimental uncertainties in the determinations of the melting point and heat of fusion, especially in the case of multiple melting endotherms. In general, groups that support *melt-recrystallization* model^{81, 91, 114} are in favor of using T_{mI} as the apparent melting temperature because it represents the melting of the original crystal before the heating scan. However, based on the modified model proposed by Lee and Porter⁵⁴, as shown in **Figure 2.8**, neither true T_{mI} nor heat of fusion could be directly determined from the DSC thermograms due to the continuous melting and recrystallization process. On the other hand, groups backing *dual lamellar population* model¹³⁰ would prefer to use T_{mI} and T_{mII} as the true melting of secondary and primary crystal. Nevertheless, both Cebe⁵¹ and Hsiao et al.⁶⁴ questioned the eligibility of T_{mII} being representative of true melting of the original morphology because it experiences lamellar thickening during the scan and contributes to endotherm II which may be independent of original primary crystals.

2.4.2 $\Delta H_m(T_m^0)$ of PLLA

In the literature, very different $\Delta H_m^0(T_m^0)$ values of PLA were reported, ranging from 93.7 J/g¹¹⁵ to 203 J/g⁴⁰. Fischer's¹¹⁵ value is probably the most widely used in the estimation of crystallinity from DSC. It was attained based on Flory's equation for the melting point depression of random copolymers (D- and L-lactides),

$$\frac{1}{T_m} = \frac{1}{T_m^\infty} - \left(\frac{R}{\Delta H_m} \right) \ln X_L \quad (2.7)$$

where T_m is the apparent melting temperature from T_mI, ΔH_m is the heat of fusion per repeating unit, X_L is the molar fraction of L-lactides. Pyda et al.¹³¹ got a similar value of 91J/g when he applied the Gibbs-Thomson equation to estimate the T_m^∞ . As shown in **Figure 2.23**, there may not be enough data points to encourage a reliable extrapolation.

Nijenhuis et al.¹³² reported $\Delta H_m^0(T_m^0)$ to be 100J/g for a slowly polymerized, ultra high crystalline, high MW nascent PLLA polymerized with catalyst Zn(DMH)₂, other than the traditional Sn(Oct)₂. A value of 106 J/g from a MS thesis¹³³ was used by Sarasua et al.³⁹ to calculate the degree of crystallinity from DSC. Although Cohn et al.¹³⁴ did not explicitly state the $\Delta H_m^0(T_m^0)$ value, it could easily be back-calculated from their calculation of calorimetric crystallinity as about 148 J/g. However, no explanation on the source of such value was provided. Jamshidi's⁴⁰ $\Delta H_m^0(T_m^0)$ value, 203 J/g, is more than double the Fischer's value (3.5Kcal/mol vs. 1.6Kcal/mol). By examining the T_m of a series of PLLAs with different MW, the plot of T_m^{-1} against M_n^{-1} is expected to give a straight line according to Flory's equation,

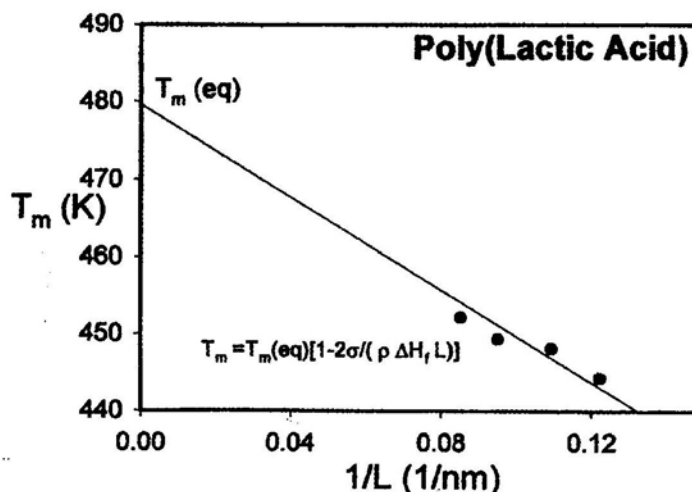


Figure 2.23 Apparent Melting Temperature vs. Inverse Lamellar Thickness of PLA Crystallized at Different Temperature¹³¹

$$\frac{1}{T_m^\infty} - \frac{1}{T_m} = \frac{2RM_o}{\Delta H_m M_n} \quad (2.8)$$

where T_m^∞ is the T_m at infinite MW, R is the gas constant, M_o is the MW of the repeat unit, and $\Delta H_m(T_m^\circ)$ is the heat of fusion per mole of the repeat unit. However, it seems from **Figure 2.24** that such a relationship holds approximately well only for PLLAs with relatively high MW.

2.4.3 Equilibrium melting temperature, T_m°

The definition of the equilibrium melting temperature has not been unified so far. Technically, three different definitions are currently in use. The first definition of equilibrium melting temperature is, according to the Flory's equation mentioned above, the highest melting temperature reached at infinite molecular weight. The second definition is based on the thermodynamic of polymer crystallization, or Gibbs-Thomson equation:

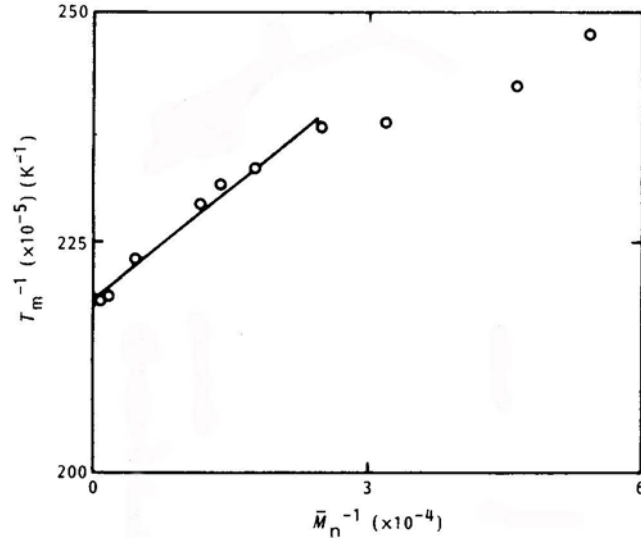


Figure 2.24 T_m^{-1} vs. M_n^{-1} for PLLA⁴⁰

$$T = T_m^o \left(1 - \frac{2\sigma_e}{\rho \Delta H_m} \frac{1}{l} \right) \quad (2.9)$$

where l is the crystalline lamellar thickness, σ_e is the lamella folding surface free energy, ρ is the density of the crystalline phase and ΔH_m is the heat of fusion per cubic centimeter. Here the T_m^o is evaluated by measuring the melting temperatures of well-defined, small crystals and extrapolating to infinitely thick crystalline lamellae ($1/l \rightarrow 0$), or extended-chain crystal.

Most commonly the equilibrium melting temperature is derived from Hoffman-Weeks¹³⁵ equation, where the relationship between melting temperature and crystallization temperature from the melt holds:

$$T_m = [T_m^o(2\beta - 1) + T_c] / 2\beta \quad (2.10)$$

where β indicates the fold length in multiples of the primary, homogeneous nucleus. When this curve intersects with curve $T_m = T_c$, T_m^o is determined from the

intersection. They defined T_m^0 as the melting point of an assembly of crystals, each of which is so large that surface effects are negligible and that each such large crystal is in equilibrium with the normal polymer liquid.

2.4.4 T_m^0 of PLLA

The equilibrium melting temperature of PLLA is reported in the literature to be 215°C³², 207°C^{33 131} and 184°C⁴⁰. Kalb³² and Vasanthakumari³³ applied Hoffman-Weeks equation to calculate their T_m^0 . Their samples are first melted at 10°C - 15°C higher than the apparent melting temperature of the materials and then cooled down rapidly to the isothermal crystallization temperatures. Kalb³² suggested a $\pm 10^\circ\text{C}$ fluctuation because the influence of lamellar thickening had been neglected. Both their plots are illustrated in **Figure 2.25** and **2.26**, respectively. Jamshidi⁴⁰, however, obtained $T_m^0 = 184^\circ\text{C}$ along with ΔH_m^0 from Flory's equation, as in **Figure 2.24**.

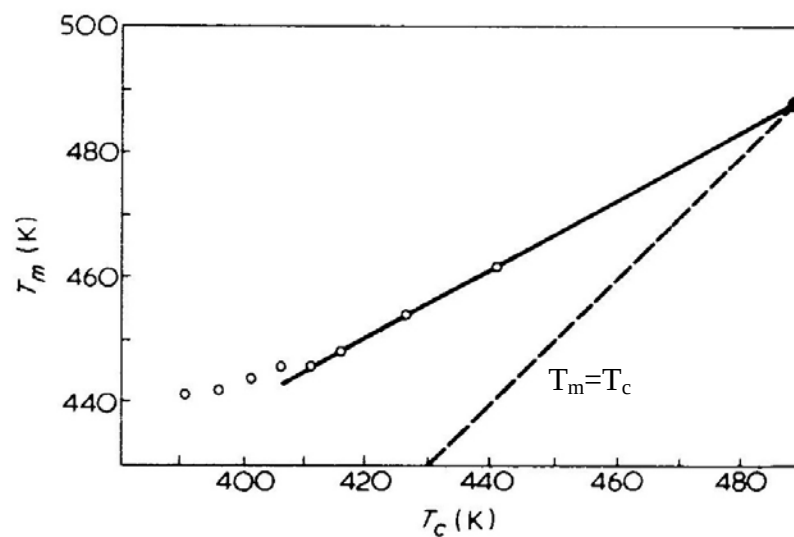


Figure 2.25 The Melting Temperature of PLLA as a Function of the Crystallization Temperature from DSC, 5°C/min³²

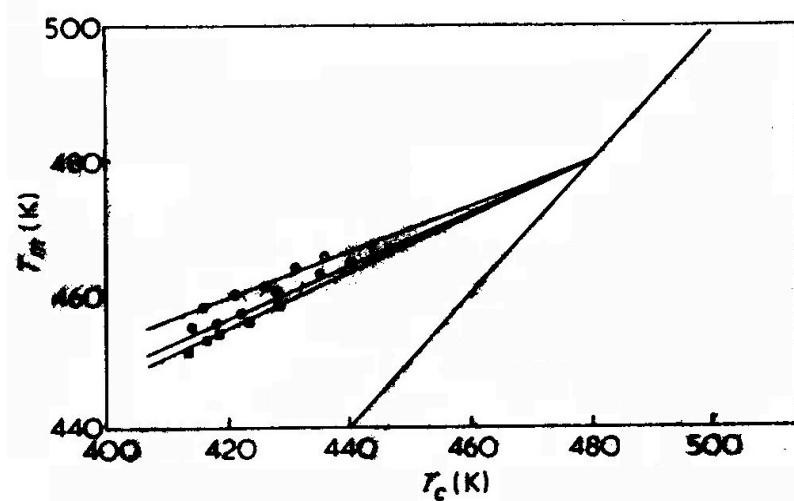


Figure 2.26 The Melting Temperature of PLLA as a Function of the Crystallization Temperature from DSC, 8°C/min, 5°C/min, 4°C/min from Top³³

CHAPTER 3 MATERIALS AND EXPERIMENTAL METHODS

3.1 MATERIALS

PLLA white virgin powder with less than 1% D-isomer was provided by Purac. The number and weight average molecular weight are 192,000 and 335,000, respectively. The PDI is narrow at 1.74. Amorphous films were compression-molded in a Wabash hydraulic press unit equipped with heating plates. Dried powders were sandwiched between a layer of Kapton film and then a layer of stainless steel platen on each side. It was first pressed at 225°C, approximately 30°C higher than its apparent melting temperature, for 5 minutes without applying any pressure to ensure the completion of melting and the equilibrium of temperature. Then a load of 1.5 tons was applied for another 5 minutes before immediately removing and cooling in an ice-water bath. The WAXD (**Figure 3.1**) and density measurements confirmed its amorphous and unoriented state. The transparent films of approximately 0.3mm thick

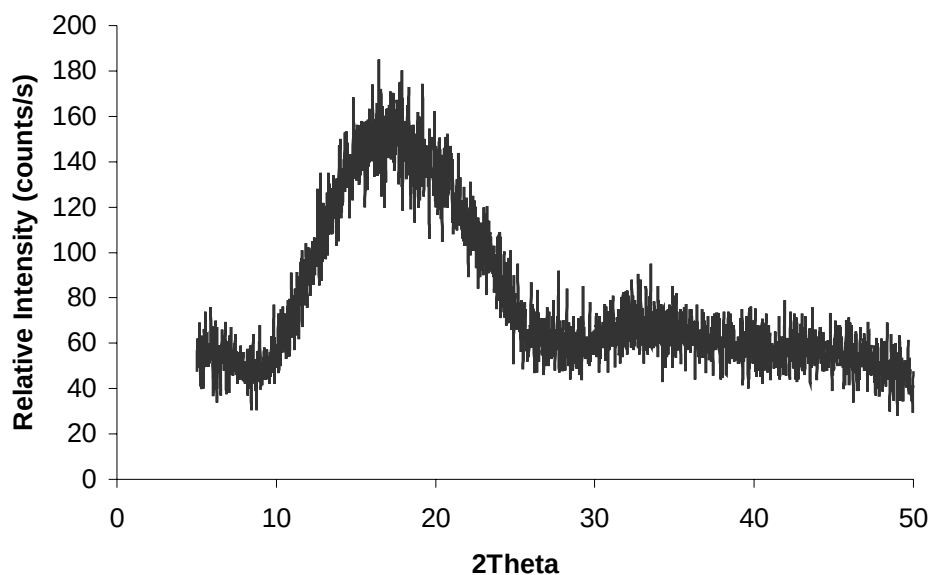


Figure 3.1 WAXD of Amorphous PLLA Film

were stored in a desiccator until further treatments were undertaken. The resultant number and weight average molecular weights of the amorphous film are 156,000 and 285,000, respectively. And the PDI become slightly higher as 1.82.

Figure 3.2 shows the DSC thermograms of both raw PLLA and PLLA in amorphous film. It is noticeable that the glass transition temperature, T_g , and the melting temperature, T_m , have decreased significantly after the film fabrication process. For comparison, another PLLA pellet sample (PLLA-C, $M_n=91.6$ k g/mol, $M_w=203$ k g/mol) from Cargill, Inc. was fabricated into films through the same procedure mentioned above, except that the temperature used was 200°C, which is also 30°C higher than its apparent melting temperature. Both T_g and T_m do not show considerable changes before and after, as in **Figure 3.3**. Interestingly, when we further examine the molecular weight changes before and after the fabrication procedure for both PLLAs, it turned out that M_n dropped 18% for PLLA, while 47% for PLLA-C. It suggests that the thermal degradation during the fabrication did not cause substantial reduction in T_g and T_m for PLLA. It is probably due to the presence of much thicker crystals in the powder PLLA samples. When quenched into amorphous films and then heated up in DSC, the crystals formed during the cold crystallization are smaller, resulting in reduction in T_g and T_m . Moreover, although T_g is associated with short-range order, while T_m with long-range order, such molecular motion should have affected T_m as well as T_g . As a matter of fact, the effect is almost the same, because the ratio between T_g and T_m (T_g/T_m) is the same before and after the film fabrication, which is 0.74.

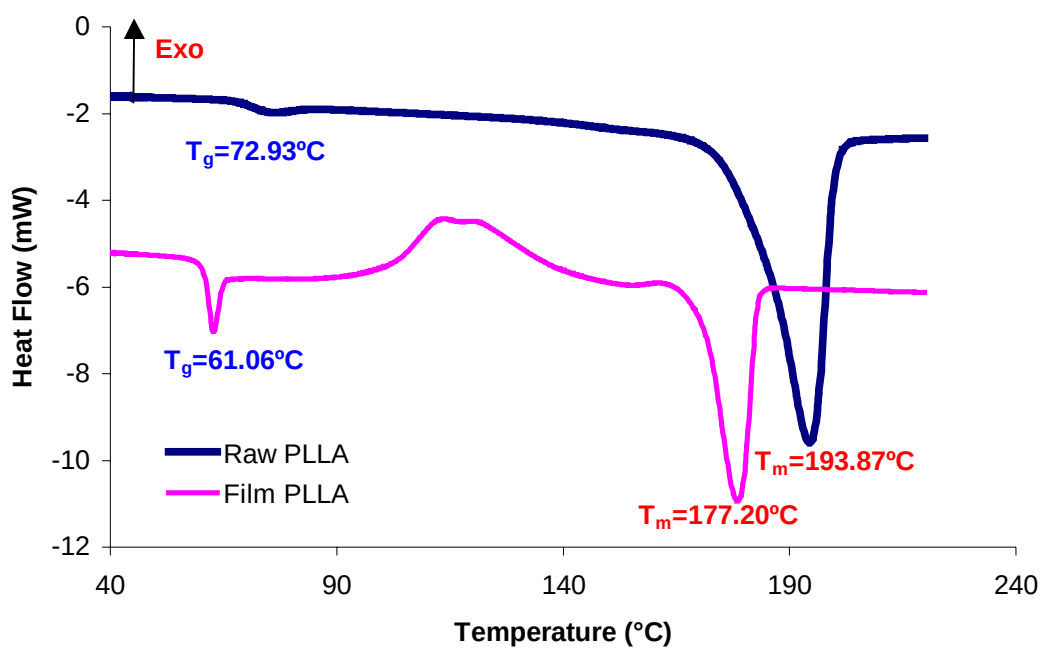


Figure 3.2 DSC Thermograms of Raw and Amorphous Films of PLLA, 10°C/min

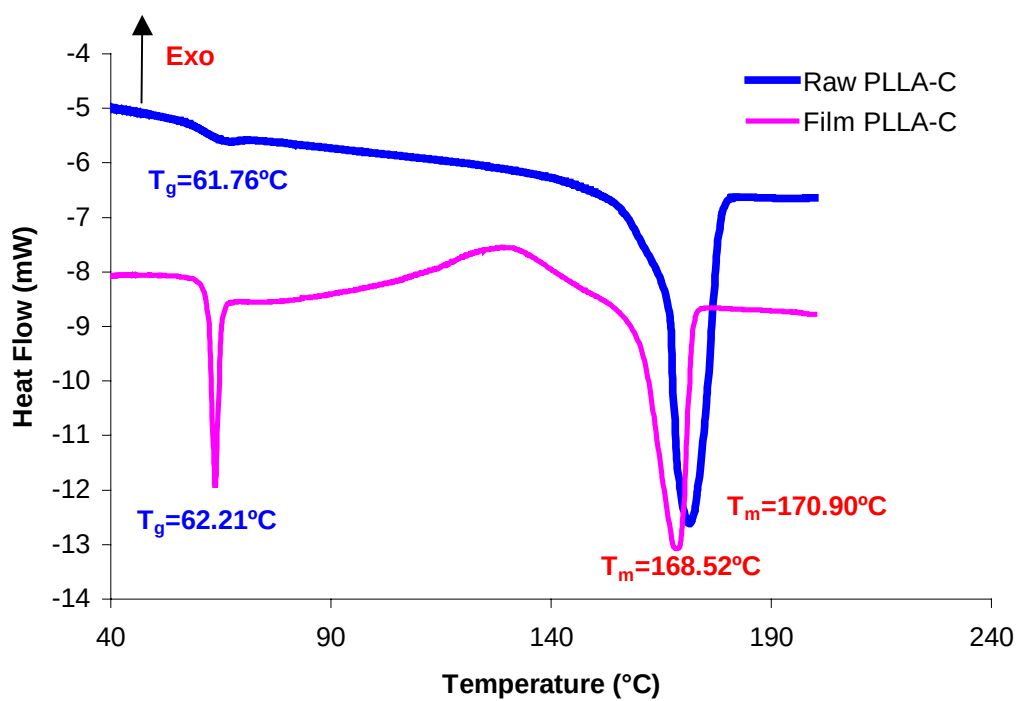


Figure 3.3 DSC Thermograms of Raw and Amorphous Films of PLLA-C, 10°C/min

3.2 CRYSTALLIZATION AND PARTIAL MELTING PROCESSES

PLLA can be crystallized either from the amorphous (glassy) state (cold-crystallization) or from the melt (melt-crystallization). Both cold-crystallization and melt-crystallization, as well as partial melting processes are achieved in the chamber of a Mettler DSC821e under controlled nitrogen purge at 200ml/min to prevent oxidation of the specimens.

3.2.1 Crystallization from the glassy state (cold-crystallization)

Isothermally cold-crystallized samples were placed in the DSC chamber which already reaches the designated temperature, T_{cc} . Upon finishing the crystallization for t_{cc} , each sample is quenched into ice-water bath immediately to preserve its crystallization state and prevent it from further crystallization.

Non-isothermal cold-crystallization was simply studied by heating the original amorphous film from 25°C to 200°C via different heating rates.

3.2.2 Crystallization from the melt (melt-crystallization)

Isothermally melt-crystallized samples were first heated from 25°C to 210°C at 10°C/min and then held at 210°C for 5 minutes to ensure complete melting. The melt was cooled at -20°C/min, where no crystallization would occur, to a designated temperature, T_{mc} . After holding a predetermined crystallization time t_{mc} , each sample was quenched into ice-water bath immediately to preserve its crystallization state and prevent it from further crystallization.

Non-isothermally melt-crystallized samples were also heated from 25°C to 210°C at 10°C/min and then held at 210°C for 5 minutes to ensure complete melting. The sample was then cooled from 210°C to 25°C at different cooling rates.

3.2.3 Partial melting

Partial melting examination was only performed on samples isothermally cold-crystallized at 100°C for 60 minutes. Each sample obtained was heated from 25°C to a certain temperature, T_{pm} , at 10°C/min in the DSC chamber before immediately being transferred into ice-water bath to memorize its crystallization state at temperature T_{pm} . The selection of T_{pm} is clearly presented in **Figure 3.4**.

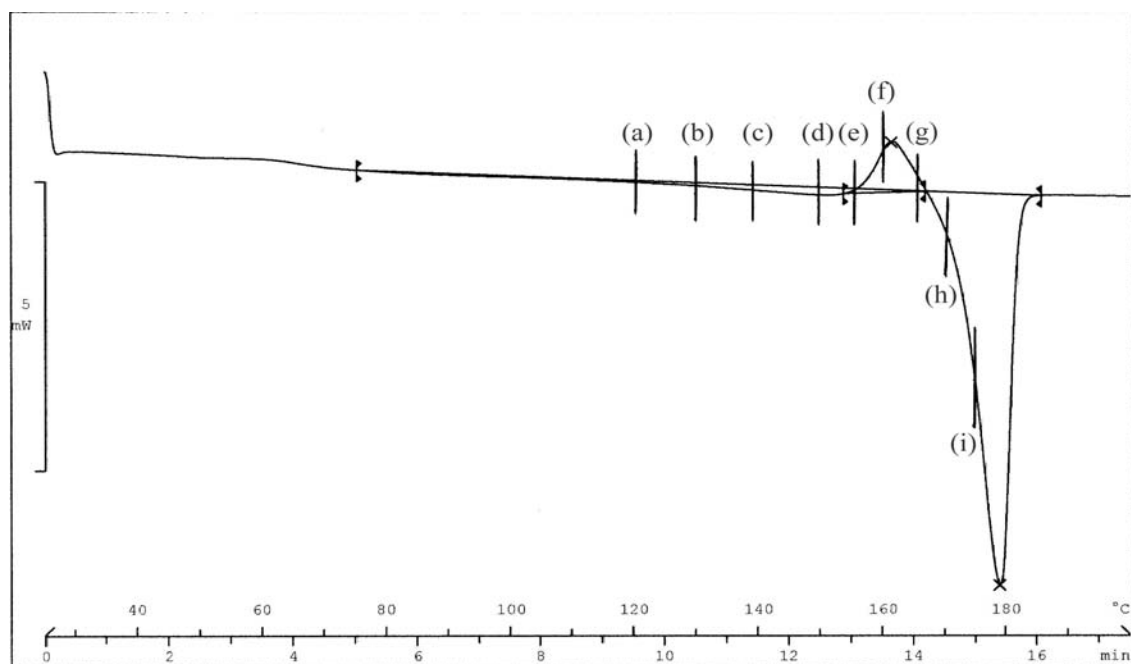


Figure 3.4 DSC Thermogram of PLLA-CC100-60min, Partial Melting Performed Where Marked (a) 120°C (b) 130°C (c) 140°C (d) 150°C (e) 155°C (f) 160°C (g) 165°C (h) 170°C (i) 175°C

3.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The melting behavior of crystallized samples was also achieved on the Mettler DSC821e under controlled nitrogen purge at 200 ml/min to prevent oxidation of the specimens. Both isothermally cold- and melt-crystallized samples, plus those partially melted samples, were heated from 25°C to 200°C at 10°C/min unless otherwise stated. Non-isothermally melt-crystallized samples were also heated up from 25°C to 200°C at different heating rates to assess the appearance of double melting peaks. The temperature and heat flow were constantly calibrated by high purity indium standard ($\Delta H=28.45\text{J/g}$, $T_m(\text{onset})=156.61^\circ\text{C}$). Care has been taken to carefully match the weights of the aluminum sample and reference pans to minimize its effect on heat capacity difference. Relatively small sample mass ($5.55\pm 0.05\text{mg}$) consisting of flat single layer polymer film was used to minimize the effect of thermal conductivity of polymers and reduce the temperature gradient.

Thermal transitions were determined by peak positions. The degree of crystallinity was conventionally calculated according to **Equation 3.1**, where $\Delta H_m(T_m)$ is the enthalpy of melting measured at melting temperature T_m , $\Delta H_c(T_c)$ is the enthalpy of crystallization measured at crystallization temperature T_c , and $\Delta H_m(T_m^0)$ is the enthalpy of fusion per mol of repeating unit of the infinite size perfect crystal/the totally crystalline polymer measured at the equilibrium point, T_m^0 , which was taken as 93J/g ¹¹⁵.

$$X_{c,h} = \frac{\left| \sum \Delta H_m(T_m) + \sum \Delta H_c(T_c) \right|}{\Delta H_m^0(T_m^0)} \quad (3.1)$$

3.4 TEMPERATURE MODULATED DSC (TMDSC)

Traditional DSC measures the heat absorbed or released by a sample as it goes through different thermal transitions. These measurements have provided valuable information regarding the physical and chemical changes that involve endothermic or exothermic processes, or changes in the heat capacity. TMDSC was first introduced by Reading¹³⁶ in 1993, and since vastly developed and understood¹³⁷⁻¹⁴¹. The principle of TMDSC is to superimpose a low frequency temperature oscillation on the linear or isothermal temperature programs often found in conventional DSC. That is, if a conventional heating program is $T = T_o + bt$, a corresponding TMDSC heating program becomes $T = T_o + bt + B\sin(\omega t)$, where T_o is the starting temperature, ω is the frequency, b is the heating rate, and B is the amplitude of temperature modulation.

The general response of both conventional DSC and TMDSC can be expressed as:

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t, T) \quad (3.2)$$

where Q is the amount of heat absorbed or released, C_p is the thermodynamic heat capacity, T is the temperature, and $f(t, T)$ is a function of time and absolute temperature. This equation clearly shows that the total heat flow, dQ/dt , which is the only heat flow measured by conventional DSC, is composed of two components: the reversing heat flow component that is relates to the sample's heat capacity and the rate of the change of the temperature, and the non-reversing heat flow component that is governed by kinetically driven processes such as physical or chemical transformations. Fourier transformation analysis is usually used to separate the experimental heat flow

into the heat capacity related (reversible) and kinetic (non-reversible) heat flows. Typical reversing events are glass transition and crystalline melting, and examples of non-reversing events are cold crystallization, evaporation, thermoset cure and decomposition.

The major advantages that TMDSC has over conventional DSC include improved resolution, enhanced sensitivity, and capability to differentiate overlapping phenomena^{136, 140}. In conventional DSC, resolution and sensitivity always have to compromise each other. However, since TMDSC is subjected to two heating rates, a faster periodic one assures good sensitivity, and a slower underlying ramp good resolution. The reversing heat flow is great for quantifying the glass transition because it separates the glass transition entirely from other non-reversing thermal events such as enthalpy relaxation and crystallization. It is also an excellent tool to study multiple melting phenomena in that exothermic events are completely absented from the reversing signal and detected only in the non-reversing signal. Unfortunately, endothermic melting behavior can contribute to both reversing and non-reversing signals and TMDSC fails to distinguish. The relative fractions depend on the experimental conditions and the types of crystals present.

A TA Q1000 temperature modulated DSC and its universal analysis software were used for TMDSC analysis. Throughout the investigation, the underlying heating rate is 1°C/min with modulation amplitude of 0.5°C and modulation period of 60s. Aluminum sample pans are kept virtually the same weight and the sample weight is approximately 5.55±0.05 mg. Calibrations for cell resistance and capacitance, cell constant and temperature were routinely performed according to TA preset program

with empty pans, sapphire and indium standards, while the heat capacity calibration constant for the modulation calibration was done using a standard sapphire sample before each scan.

3.5 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis is a thermal analysis technique that measures the weight (mass) changes of a substance as a function of temperature and/or time. Typical results of TGA of polymers can reveal degradation temperatures, moisture contents, residual solvent levels, and material compositions.

A sample is first placed into a tared 900 μ l aluminum oxide cubicle, and then carefully positioned in Mettler TGA/DSTA851e that is equipped with a sensitive microbalance assembly. Once the sample is enclosed in the high temperature furnace and heating program starts, the balance continuously measures and records the weight changes. In our research, TGA of amorphous film is scanned from 25 to 600°C at a heating rate of 10°C/min, also holding isothermally at 210°C for 240 minutes. Each scan is performed under 80ml/min nitrogen purge. Indium/Aluminum was used to calibrate over the whole temperature range.

3.6 DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic mechanical analysis measures the stress, strain and their phase angle (δ) of materials while they are subjected to a sinusoidal stress. It is particularly useful

for measuring transitions in polymers that cannot be detected by other techniques, and studying polymer blends.

Dynamic mechanical analysis was carried out in tensile mode on the Rheometric Scientific DMTAV operated with the 1Hz frequency and temperature ramp from 30°C to 140°C at 1°C/min. The spring constant was always calibrated before each measurement. Films are cut in the form of strip about 7mm in width. Strain is set to be 0.1%.

3.7 SMALL ANGLE X-RAY SCATTERING (SAXS) AND WIDE ANGLE X-RAY DIFFRACTION (WAXD)

Samples taken out of the DSC pans can be examined in the Molecular Metrology SAXS/WAXD system as is. This system is equipped with a monochromic CuK α (1.5418 Å) x-ray source, a three-pin-hole alignment and a two-dimensional detector. It normally operates at 45kV and 0.66mA and the beam size is ~30 μ m. The sample-to-detector distance is 1.5m for SAXS measurement. A Matlab program was designed and provided by the manufacturer for analysis purpose. Lorentz corrected intensity is then plotted against q and the long period ($L_{\max}$) and corresponding lamellar thickness (l_c) are calculated by the following equations, where $X_{c,h}$ is the degree of crystallinity derived from DSC.

$$L_{\max} = \frac{2\pi}{q_{\max}} \quad (3.3)$$

$$l_c = L_{\max} \times X_c \quad (3.4)$$

This system also has the capacity of recording WAXD patterns onto reusable Fuji image plates, where the sample-to-film distance is 36.52mm. The image plate can be scanned in a FujiX BAS-1800II image analyzer and the resultant image then deconvoluted to a 2θ vs. intensity plot using a Polar program. All curves were normalized and shifted for better presentation.

3.8 GEL PERMEATION CHROMATOGRAPHY (GPC)

The molecular weights of the samples were analyzed using a Polymer Labs GPC-220 size exclusion chromatograph. It contained three Polymer Labs PLgel 10 μ m MIXED-B columns running chloroform as the solvent at a flow rate of 1ml/min at 40°C. Polystyrene standard was used for calibration purpose. The analysis was performed using Precision Detector Cirrus software.

3.9 DENSITY GRADIENT COLUMN (DGC)

According to ASTM D1505 – “Standard Test Method for Density of Plastics by the Density Gradient Technique”, water-sodium bromide liquid systems targeting density range from 1.00 – 1.41 g/cm³ was selected because the density of PLLA is around 1.25 g/cm³. A high-density solution and a low-density solution of water and sodium bromide was prepared according to the desired testing range, which is 1.24 – 1.28 g/cm³ in this case. A density column with smooth gradient was made by pouring these two solutions gradually. A Haake N3-R constant-temperature circulator was connected to the column, maintaining it at 23 $\pm$ 0.1°C. Four standard glass beads of density of 1.245, 1.255, 1.265, 1.275 g/cm³ were placed into the column for

calibration. The equilibrium position was recorded after 24 hrs and a linear calibration plot of height versus density was generated. Then samples were wetted in the low-density solution first before putting them into the density gradient column. Height positions of samples were read off the scale of the column after 24 hrs equilibrium and the density value was converted from height measurements according to the calibration plot in **Figure 3.5**. In order to calculate the equilibrium heat of fusion, prior knowledge of the density of 100% crystalline PLLA is also needed. Here we used $\rho_c = 1.2762 \text{ g/cm}^3$ based on our previous research ⁷.

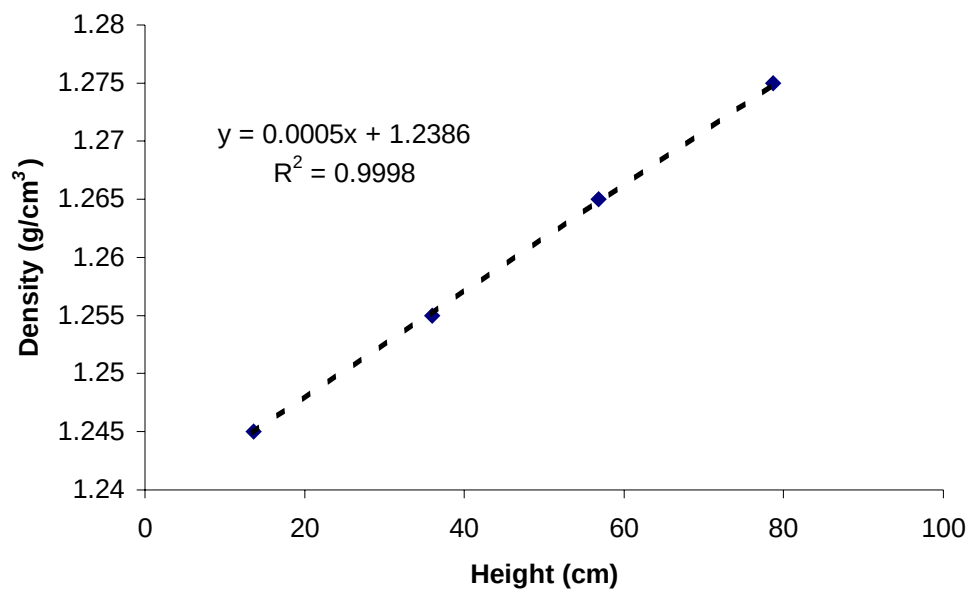


Figure 3.5 Calibration Curve of the Density Gradient Column for PLLA

CHAPTER 4 SAMPLES CRYSTALLIZED FROM GLASSY STATE

4.1 NON-ISOTHERMAL CRYSTALLIZATION FROM THE GLASSY STATE

When the amorphous film is heated up in the DSC from 25°C to 200°C at 10°C/min, a T_g at 62°C followed by a double cold-crystallization peak at $T_{cI}=112^\circ\text{C}$ and $T_{cI'}=119^\circ\text{C}$ is observed, as illustrated in **Figure 2.4**. Double cold-crystallization is not observed when heating rate is lower (1, 2.5 and 5°C/min) or higher (20°C/min), as shown in **Figure 4.1**. Another exotherm, T_{cII} appears just prior to the final melting. While the position of T_{cII} and T_m remains virtually the same, ΔH_{cII} decreases with increasing heating rate.

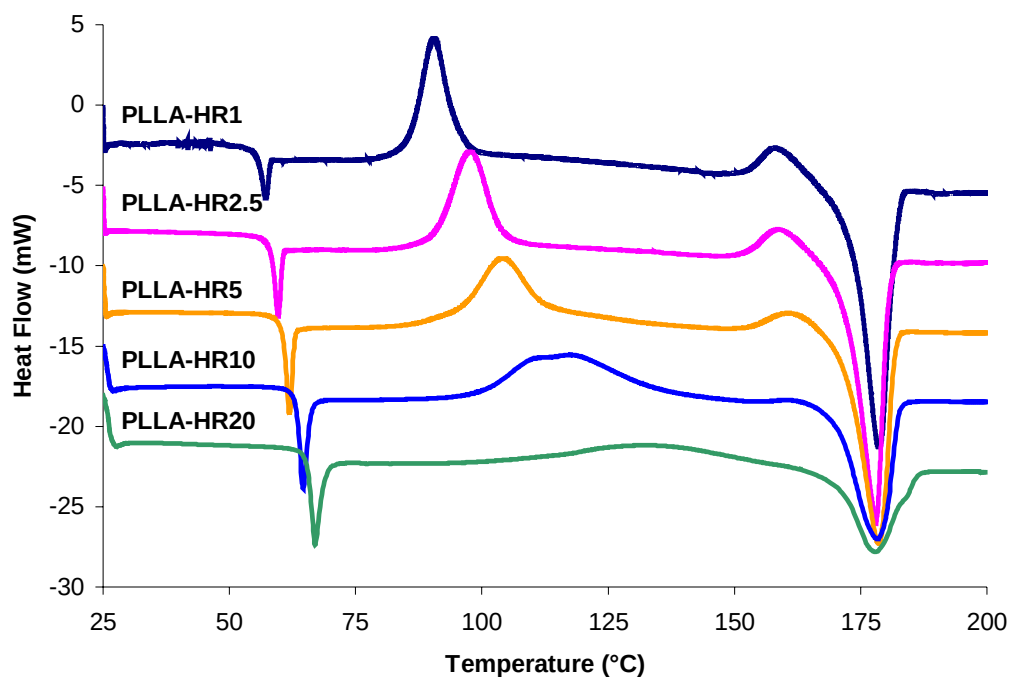


Figure 4.1 DSC Thermograms of Amorphous PLLA Film Scanned at Different Heating Rates

The observation of T_{cI}' is possibly due to the onset of melting and recrystallization of the unstable crystals that begins before the cold-crystallization is even completed. The double cold-crystallization peak is therefore the net effect of cold-crystallization and melt-recrystallization of the unstable crystals formed during the original cold-crystallization. This is especially pronounced when our PLLA has high molecular weight and a narrow PDI, where most polymer chains consist of quite long sequences. At lower heating rate, as shown in **Figure 4.1**, the cold-crystallization had longer time to complete and the crystals formed are more stable, so that the onset of melt-recrystallization would not have strongly competed with the cold-crystallization and recrystallization only occurs in T_{cII} . On the other hand, at higher heating rate, the initial crystals are less stable and begin to recrystallize immediately during the cold-crystallization, appearing as an overall broad peak and there will be no T_{cII} peak. Migliaresi et al.¹¹⁷ have observed similar shape in cold-crystallization peak in PLLA with high molecular weight ($M_w=425,000$ g/mol) as well.

Temperature modulated DSC of the amorphous film was conducted at $1^\circ\text{C}/\text{min}$, as seen in **Figure 4.2**. The red curve is the total heat flow vs. temperature, which is consistent with the regular DSC scan at the same rate shown in **Figure 4.1**. The green curve represents the reversing heat flow vs. temperature. When plotted in the same scale with total heat flow and non-reversing heat flow, the details of this curve are obscured. When plotted on an expanded scale in **Figure 4.3**, a sharp T_g at 60°C is observed, along with a small exothermic signal occurring around 96°C . This

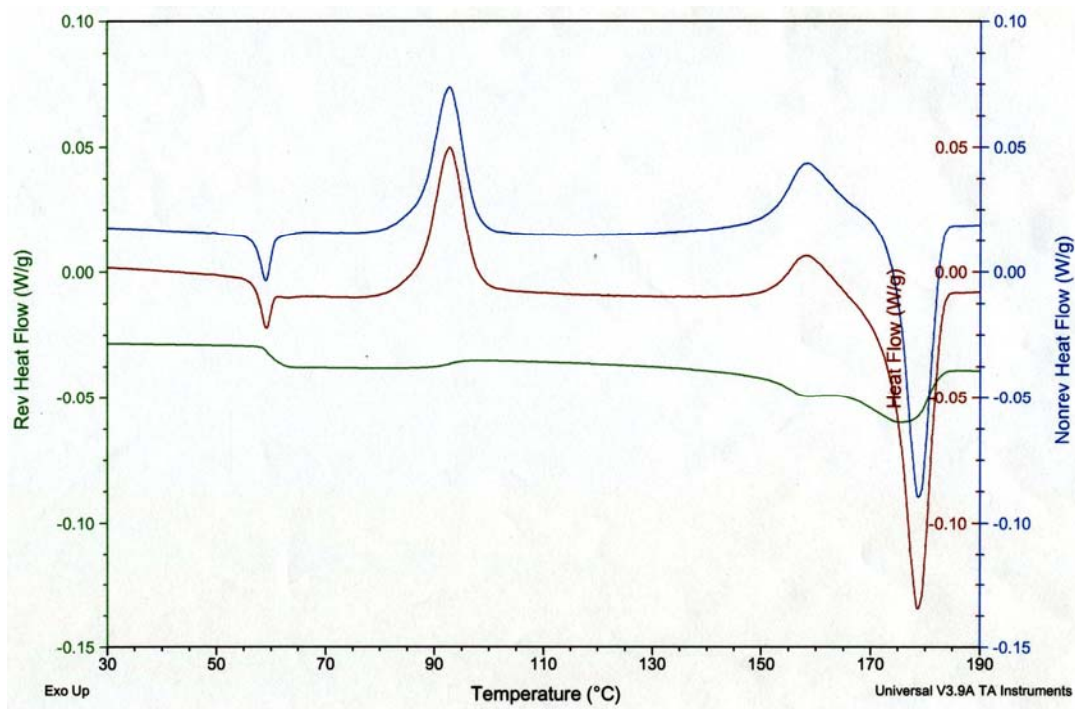


Figure 4.2 Total, Reversing, Non-reversing Heat Flow of Amorphous PLLA Film vs. Temperature at 1°C/min, with 0.5°C Amplitude and 60s Period from TMDSC

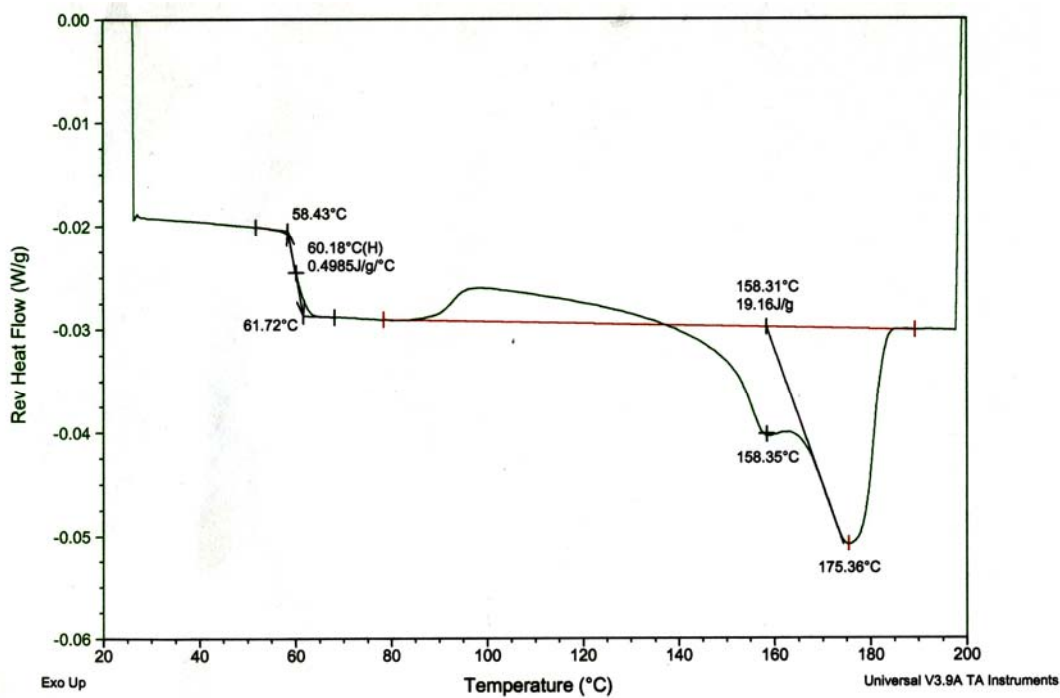


Figure 4.3 Reversing Heat Flow vs. Temperature from Figure 4.2

exothermic peak cannot be regarded as due to crystallization, which is a non-reversible process. Instead it is a slight shift of vibration heat capacity due to an increase of crystallinity during the cold-crystallization, which is followed immediately by the onset of melting. Two melting peaks, located at 158.35°C and 175.36°C, are observed, the first one being the melting of unstable crystals. Finally, the blue non-reversing curve represents the difference between the total and reversing heat flow. It shows an enthalpic relaxation at 59.03°C, which is related with the relaxation of strain accumulated during the quick quenching process of making amorphous film. An exotherm, T_{cII} , occurred at 158.35°C, corresponding to the first melting peak, T_{mI} , in reversing curve. This indicates that the melting and recrystallization take place almost simultaneously. Final non-reversing melting occurred at 178.62°C. Standard DSC only reveals the offsetting of endothermic and exothermic signals. When recrystallization overwhelms melting, only an exothermic peak, T_{cII} , is shown, as in our amorphous PLLA film, i.e. instead of showing $T_{mI}+T_{mII}$, $T_{cII}+T_{mII}$ appears in the DSC curve. Such obscurity is overcome by TMDSC analysis. Also the coexistence of crystallization and reorganization during melting can lead to a degree of reversibility in the melting as presented in the reversing component of the melting peak. Overall, at heating rate 1°C/min, even the onset of melting and recrystallization occurs before the crystallization is completed, as shown in **Figure 4.2** the overall extent is not significant enough to cause the appearance of double cold-crystallization as is observed at heating rate 10°C/min.

DMA data acquired at the same heating rate, 1°C/min, is shown in **Figure 4.4**. Both the storage modulus and $\tan\delta$ curves clearly exhibit the relaxation associated with only one glass transition at about 68°C, which excludes the existence of two different amorphous states in the starting material. The modulus also increases in the range 85°C-100°C due to the development of crystallinity. Of particular significance is the presence of a small, but repeatable peak in the $\tan\delta$ curve at about 95°C. This recorded peak temperature is in line with the distinguished heat capacity change observed at 96°C in TMDSC shown in **Figure 4.3**, which indicates the onset of the melt-recrystallization. It changes the overall crystallization rate, or the rate of modulus or crystallinity enhancement.

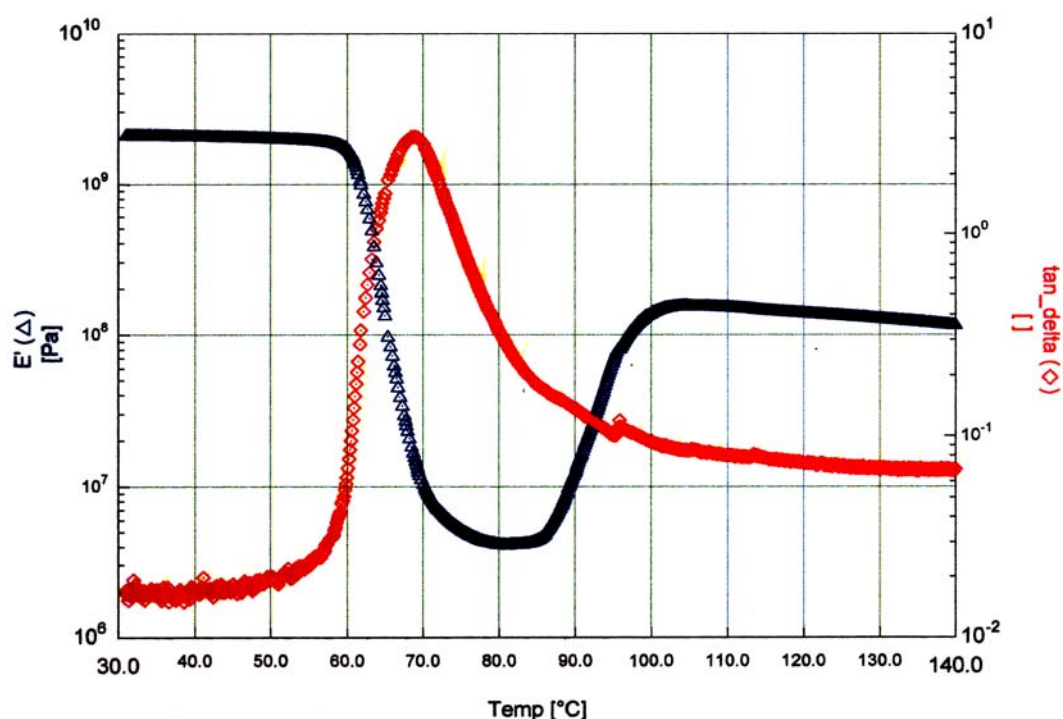


Figure 4.4 DMA of PLLA Amorphous Fil at 1°C/min Ramp and 1Hz Frequency in Tensile Mode

A quick look at crystallization rate ($t_{1/2}$) as a function of crystallization temperature in **Figure 4.5** shows the maximum crystallization rate occurs around 100°C. This is in close agreement with 105°C reported by other groups^{35, 38}. It seems that from 96°C to around 100°C in **Figure 4.4**, E' is still on the rise despite the onset of melt-recrystallization process. The overall crystallization rate (cold-crystallization plus recrystallization) in this range is faster than the rate of melting of metastable crystals, although the melting slows down the development of E'. Above 100°C, as the overall crystallization rate starts to decrease, E' drops gradually as temperature continues to rise.

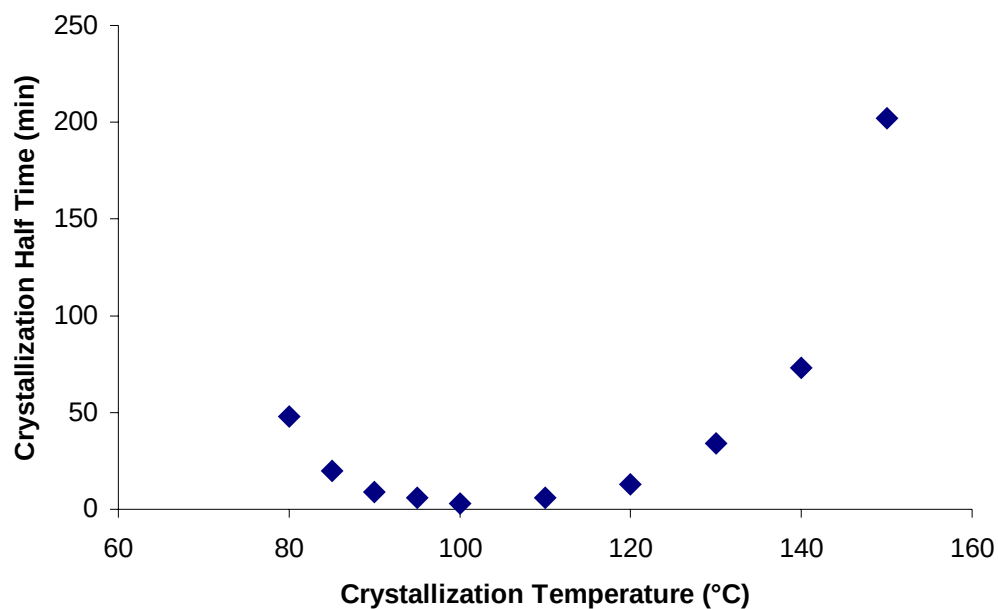


Figure 4.5 Crystallization Rate vs. Crystallization Temperature of PLLA Amorphous Film

In addition, the suggestion by Yang et al.⁴⁶ on the possible origin of double cold-crystallization from the lowered surface energy of crystallization due to moisture does not seem to apply to our PLLAs, which is securely stored in the desiccator. This can be proved from **Figure 4.6**, where no peak is detected around 100°C in the first derivative curve. Therefore TGA of the amorphous film shows no significant weight loss from the moisture content.

Using simultaneous SAXS and WAXS and Avrami parameter analysis, Mano et al.¹⁴² concluded 3-D growth during the non-isothermal cold crystallization for the amorphous PLLA, although an imperfect crystallization process was involved at early times ($n < 3$). This is similar to what Lu et al.⁴⁵ found for PET fibers, which they used to explain the double cold-crystallization phenomena. However, the adaptation of Avrami equation to study non-isothermal events is still somewhat debatable.

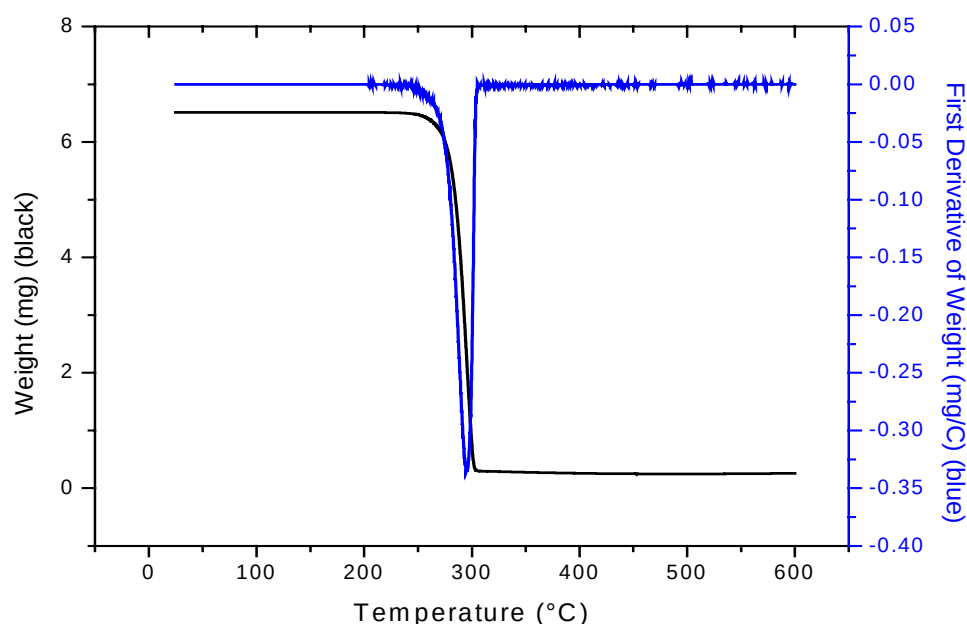


Figure 4.6 TGA Thermogram of PLLA Amorphous Film and Its First Derivative

4.2 ISOTHERMAL CRYSTALLIZATION FROM THE GLASSY STATE

4.2.1 Samples crystallized at different temperature for 1 hr

In order to examine the effect that cooling (quenching into ice-water) might have on the subsequent DSC scans, selected samples were heated directly from T_{cc} to 200°C at 10°C/min for comparison. As illustrated in **Figure 4.7**, there is no distinctive variation between these two different procedures in the temperature range of interest. There is no extra endotherm caused by possible crystallization during the cooling, as observed and reported in other polymer systems^{57, 58, 77, 78}, even when T_{cc} is fairly close to the T_m . Thus, the possibility of T_mI of double melting peaks that stems from crystallization during cooling can be safely ruled out.

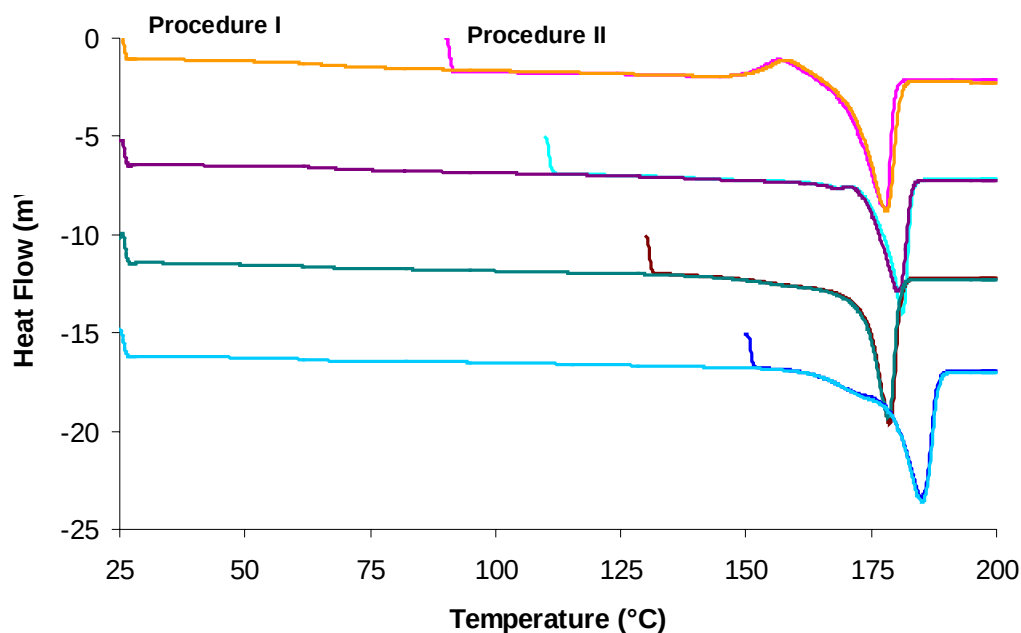


Figure 4.7 DSC Thermograms of Isothermally Cold-crystallized Samples with Different Procedures (Procedure I: heating from 25°C to 200°C after quenching, and Procedure II: heating directly from T_{cc} to 200°C, at 10°C/min. From top to bottom, T_{cc} is 90°C, 110°C, 130°C and 150°C)

After each amorphous PLLA film is cold-crystallized at different temperatures, from 80°C to 160°C with an increment of 10°C, for 1 hr, their subsequent DSC thermograms are illustrated in **Figure 4.8** and the temperatures of the major effects are summarized in **Table 4.1**. The crystallization did not complete in 60 minutes at 80°C (PLLA-CC80), showing a broad exothermic cold-crystallization peak, T_{cI} , above the baseline, which is substantially less intense than the cold-crystallization peak in the as-pressed amorphous film, as in **Figure 2.4**. The curves of PLLA-CC80, 90 and 100, also exhibit the second crystallization peak, T_{cII} , just prior to final melting, T_{mII} , as confirmed previously by TMDSC analysis. (T_{mI} is not shown in conventional DSC after treatment at these temperatures because the net effect of melting and recrystallization is exothermic instead of endothermic.) T_{cII} serves as a distinctive indicator of the intensive melt-recrystallization process the sample is experiencing during the heating scan due to the continuous reorganization of ill-formed crystals. The melting and recrystallization of imperfect crystals starts almost simultaneously and so competitive to each other that T_{mI} does not show up at all, which is only detected by TMDSC, as demonstrated previously in **Figure 4.2**. The T_{cII} peak temperature gradually moves from 156.45°C to 157.93°C to 161.44°C, while ΔH_{cII} decreases slightly, as the recrystallization subsides with slightly more stable initial crystals formed at a higher treatment temperature. However, such change is not obvious compared with what have been observed in other polymers, which is probably due to the close competition between melting and recrystallization of PLLAs.

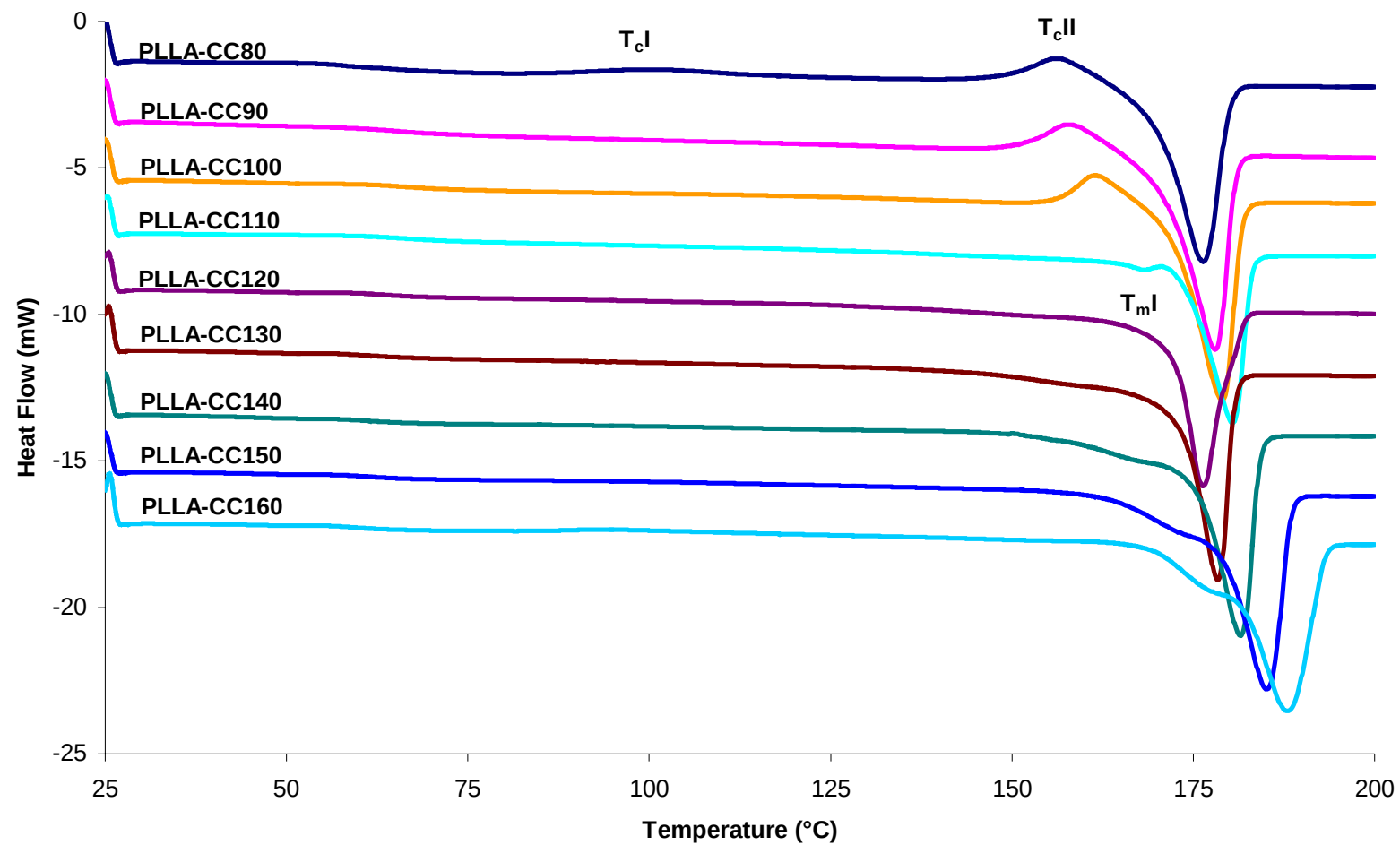


Figure 4.8 DSC Thermograms of PLLA Cold-crystallized at Different Temperature for 60 minutes, 10°C/min

Table 4.1 Summary of Observed Thermal Effects of PLLA Cold-crystallized at Different Temperatures for 1 hr (°C) and the Degree of Crystallinity

	T_{cI}	T_{mI}	T_{cII}	T_{mII}	$X_{c,h}$ (%)
PLLA-CC80	100.93	-	157.10	176.76	33.9%
PLLA-CC90	-	-	157.93	177.58	43.9%
PLLA-CC100	-	-	161.44	178.59	48.3%
PLLA-CC110	-	168.06	-	179.98	53.7%
PLLA-CC120	-	175.97	-	-	54.5%
PLLA-CC130	-	177.92	-	-	58.1%
PLLA-CC140	-	*	-	181.08	65.0%
PLLA-CC150	-	*	-	184.75	66.4%
PLLA-CC160	-	*	-	187.64	65.4%

* a small shoulder precedes the final melting.

The DSC scan of PLLA-CC110 shows apparent double melting peaks at $T_{mI}=168.06^{\circ}\text{C}$ and $T_{mII}=179.98^{\circ}\text{C}$, with the ΔH_{mII} significantly larger than that of ΔH_{mI} . Most crystals formed at 110°C can still be unstable and underwent melt-recrystallization process. However, the crystals formed are relatively more perfect and the recrystallization process slows down. Consequently, in the competition of melting and recrystallization of the imperfect crystals, the rate of melting finally overwhelms that of recrystallization at this stage, showing $T_{mI}+T_{mII}$. It is noteworthy that the small yet observable T_{mI} does not appear at $10\text{-}20^{\circ}\text{C}$ above crystallization temperature as reported in many other polymers that go through multiple melting, but almost 58°C higher than its T_{cc} . This could be due to the competition between the melting and recrystallization being so close that the melting does not have absolute advantage until much higher temperature is reached where recrystallization rate eventually slows down. T_{mII} of samples cold-crystallized from 80°C to 110°C increases, so does the crystallinity, as more perfect crystals are generated during the heating scan.

DSC curves of samples treated at $T_{cc}=120^{\circ}\text{C}$ and 130°C shows only a single melting peak, T_mI , indicating the complete melting of original crystals without reorganization at $10^{\circ}\text{C}/\text{min}$. For samples crystallized at elevated T_{cc} (140 , 150 , and 160°C), a broad shoulder appears before the major melting. The higher the cold crystallization temperature, the more obvious this shoulder becomes. This appearance of such double melting curve is most likely due to the existence of dual lamellar population in these cold-crystallized samples, which will be further confirmed by SAXS patterns. Also, at high cold crystallization temperature, the crystals formed are thicker and more perfect, leading to significant increase in the final melting temperatures. In fact, the final melting point of samples cold-crystallized at 160°C reaches 187.64°C , almost 10°C higher than that of the original amorphous PLLA films after cold-crystallization during the DSC scan.

As we recall, the DSC curve of PLLA amorphous film has “cold-crystallization” peaks, T_cI and T_cI' , at around 112°C and 119°C , as in **Figure 2.4**. Taking that into consideration, it seems that samples treated between the glass transition temperature and cold-crystallization temperatures of the amorphous film, produce poorer, less stable crystals. During the subsequent heating scan, most of these poor crystals undergo a continuous melt-recrystallization process to form larger crystals with better perfection; the existence of exothermic T_cII serves as strong evidence. On the other hand, when treated between cold-crystallization temperatures and the melting temperature of the amorphous film, the crystals formed are more

perfect so that T_{cII} is not observed, but a single melting temperature, T_{mI} , at 10°C/min.

Ohtani et al.¹²³ recently reported T_{cI} , T_{cII} from their amorphous PLLA with molecular weight of 100,000 g/mol. They also observed a discontinuity at 120°C when the major melting points of treated samples are plotted as a function of the corresponding cold-crystallization temperatures. Here major melting point is described as the strongest peak of each DSC curve. Admittedly, their overall observations are very similar to ours regardless of the difference in molecular weights, if we plot only the major melting peak against T_{cc} and overlook the possible melt-recrystallization event, as in **Figure 4.9**. We believe the discontinuity is due to the inconsistency of melting points plotted. That is, due to the continuous melt-recrystallization, the major melting points plotted for samples cold-crystallized below 120°C is actually T_{mII} , while that plotted for samples cold-crystallized at 120°C is T_{mI} .

From their wide-angle x-ray patterns **Figure 2.22**, Ohtani and coworkers¹²³ claimed that when amorphous PLLA was crystallized at a temperature below 120°C, crystallites of the β -form formed based on the absence of reflection (103) and (011), and when annealed at a temperature higher than 120°C, crystallites of the α -form grew. Thus, T_{cI} was attributed to cold-crystallization of the β -form, and T_{cII} was caused by the phase transition of the β -form to a more stable form. Although they also claimed that the DSC curves are complicated, e.g., a multiple endothermic peak exists on annealing in the temperature range from 105°C to 120°C, and a shoulder

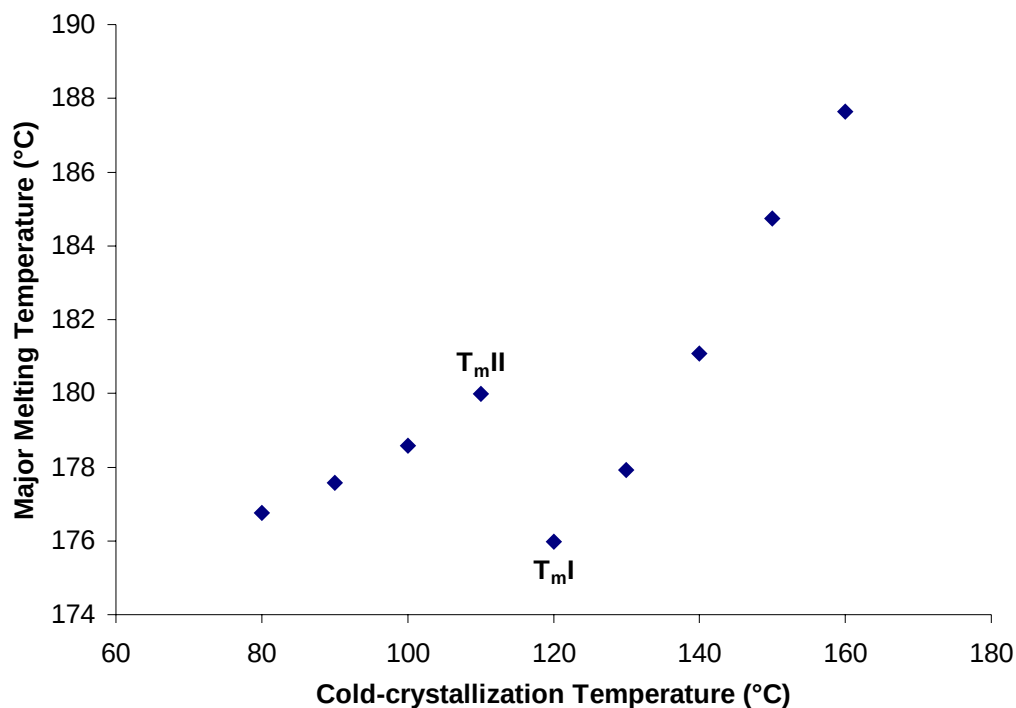


Figure 4.9 Major Melting Temperature as a Function of Cold-crystallization Temperatures of Cold-crystallized PLLAs

appears around the melting peak by annealing over 120°C, their focus was said to be just on the major melting points. As a result, they observed a sudden drop of T_m at $T_{cc}=120^\circ\text{C}$ before it increases again, which they claim is due to different phases below and above the temperature of 120°C.

β - crystal modification of PLLA was first prepared by Eling et al.¹⁷ in fibers solution-spun from semidilute toluene and then hot-drawn to high draw ratio and temperature close to T_m . At low draw ratio, fiber consists almost exclusively of α -crystal. Leenslag and Jennings¹⁴³ and Hoogsteen et al.¹⁶ both achieved fibers with only β -crystal by hot-drawing solution-spun PLLA fibers at certain extreme

conditions. They also reported that fibers consisting of β - crystal modification alone could only be prepared by the drawing of solution-spun fibers of high molecular weights under drawing conditions leading to inhomogeneous draw. In spite of that, Sawai et al.¹⁴⁴ recently prepared oriented PLLA rods consisting of only β -crystals by solid-state extrusion of billets containing only α -crystals. It seems so far that the β -crystals are mostly achieved when the samples were highly oriented. With exception, Brizzolara et al.¹² had tried to simulate the powder patterns of both α - and β -crystals, but their proposed lattice constants were very different from others. Therefore, there is no existing report on β -crystal observed in bulk PLLA and in the absence of deformation. Based on the above literature, we could not comprehend the possibility that β -crystal simply forms in the fast quenched amorphous PLLA film without applying high temperature and high tension.

In our study, however, regardless of the presence of single or double melting peak, all the X-ray patterns of each sample indicate the existence of mainly α -crystal, as demonstrated in **Figure 4.10**. Detailed indexing can be found elsewhere⁷. Using simultaneous WAXD and SAXS measurements, Mano et al.¹⁴² were also able to observe α -crystals during non-isothermal cold-crystallization of amorphous PLLA over 90°C. Four major peaks detected are $2\theta=16.5^\circ$ (200)/(110), $2\theta=18.5^\circ$ (203), $2\theta=23.9^\circ$ (015) and $2\theta=14.8^\circ$ (010) with descending relative intensity. **Figure 4.10** shows very little detail, except for the two main peaks, for samples that were conditioned at $T_{cc}<110^\circ\text{C}$, whose DSC thermograms coincidentally exhibit an obvious exothermic peak, T_{cII} , prior to final melting. At $T_{cc}=110^\circ\text{C}$, peaks such as (103),

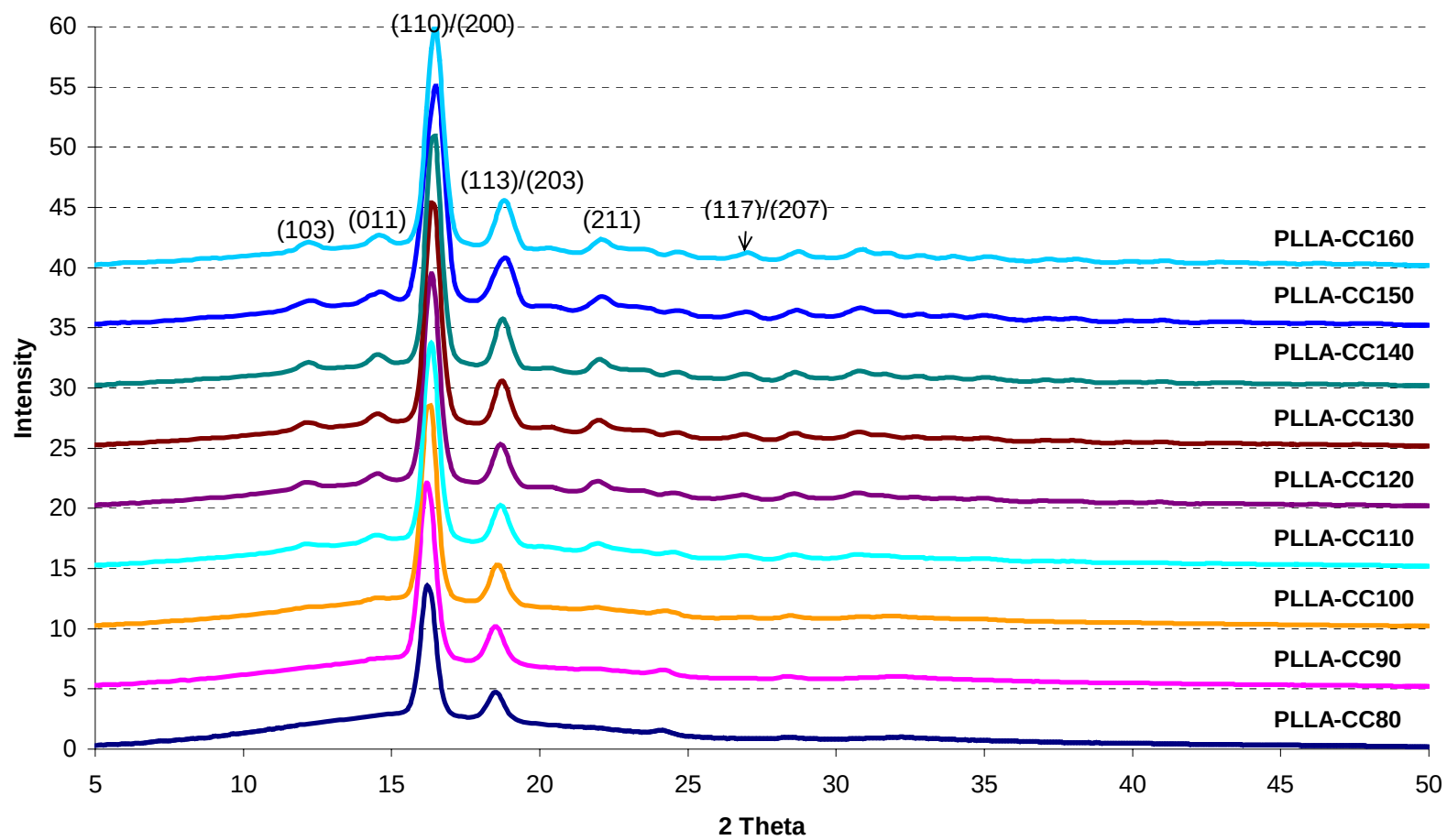


Figure 4.10 WAXD Patterns of PLLA Cold-crystallized at Different Temperature for 60 minutes

(011) and (211) start to show. As T_{cc} continues to increase, more reflections start to show and their intensities continue to develop as the crystallinity increases. It seems that crystals formed at $T_{cc} > 110^{\circ}\text{C}$ are more perfect compared with those formed at $T_{cc} < 110^{\circ}\text{C}$. Meanwhile, the absence of (103), (011) reflections may occur just because crystals formed at lower temperature are so small that their peaks have faded into the background; and not an indication of β -crystals as suggested by Ohtani et al.¹²³. Interestingly though, as the peak intensities continue to increase, the full width half maximum (FWHM) of the peaks do not show any noticeable changes, i.e. the perfection of the crystals is not simply a matter of crystal size as indicated by the WAXD peak breadths. This suggests an increasing crystallinity with increase in T_{cc} , as confirmed also by DSC results listed in **Table 4.1**. Also note that T_cII appears even when the crystallinity is close to the neighborhood of 50%.

Although we do not completely agree with Ohtani et al.¹²³ that β -crystal formed when crystallized below 120°C , we do not exclude the possibility of the formation of a mixture of α -crystals and crystals in another form in the cold-crystallized PLLA films. A close examination of **Figure 4.10** reveals a peak at around $2\theta = 24.5^{\circ}$ that remains almost unchanged in intensity while other peaks keep developing with increasing treatment temperatures. It is worth pointing out that such a peak is also observed by Ohtani et al.¹²³, as in **Figure 2.22(b)**. The exact nature of this peak is not clear at this time. Based on detailed indexing from Hoogsteen et al.¹⁶, there is no strong peak of β -phase that would appear at this particular 2θ location. Therefore, we would call it δ -crystal just to distinguish it from other reported crystal

structures. This may just be a distorted form of α -crystal, although not reported previously. Our best presumption is that there exists the mixture of major α -crystals and limited δ -crystals in the cold-crystallized samples, and the amount of δ -crystal does not change with temperature. It seems that such δ -crystal exists even when treated at a high temperature as 160°C, so that the transformation from δ -crystal to α -crystal in subsequent DSC scan would not be possible as least below 160°C. Whether the transformation takes place above 160°C is not clear to us at this time.

SAXS patterns derived from the same samples used in WAXD are detailed in **Figure 4.11** and **Table 4.2**. Long period is calculated from the peak positions. Multiply it by the DSC crystallinity, the crystalline thickness is also obtained. It seems, in **Figure 4.12**, that both long period and crystalline thickness first increase slowly when the cold crystallization is low, and then increase substantially at higher cold crystallization temperatures. At higher cold-crystallization temperature, e.g. PLLA-CC160, another long period is observed at a higher q value, indicating the existence of possible dual lamellar population structure. This observation corresponds to the broad shoulder that was seen in the DSC curves of the same sample. It is interesting that the first obvious long distance developed in samples cold-crystallized at 100°C for 60 minutes, and no periodic structure developed for samples treated at 80°C and 90°C. This is in spite of the fact that there is substantial crystallinity developed as demonstrated in **Figure 4.10** and **Table 4.1**, where the crystallinity reaches approximately 44%. This could be due to the scattering of a large number of very small crystals that do not form periodic lamellae structure.

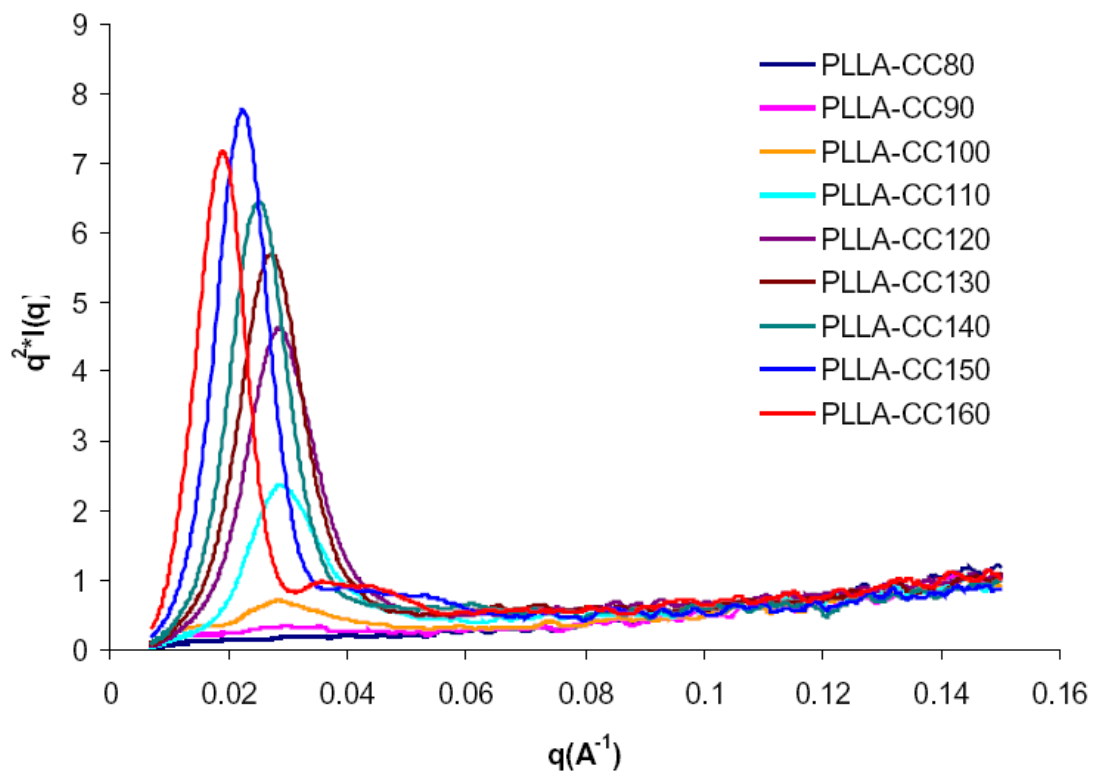


Figure 4.11 Lorentz Corrected SAXS of PLLA Cold-crystallized at Different Temperature of 60 minutes

Table 4.2 Lorentz Corrected Long Period and Lamellae Thickness of PLLA Cold-crystallized at Different Temperatures for 1 hr

	$q_{\max}(\text{\AA}^{-1})$	$L_{\max}(\text{\AA})$	$l_c(\text{\AA})$
PLLA-CC80	-	-	-
PLLA-CC90	-	-	-
PLLA-CC100	0.028131	223.35	107.90
PLLA-CC110	0.028645	219.35	117.88
PLLA-CC120	0.028656	219.26	119.56
PLLA-CC130	0.027256	230.52	134.00
PLLA-CC140	0.025173	249.60	162.24
PLLA-CC150	0.022408	280.40	186.35
PLLA-CC160	0.019104	328.89	215.03

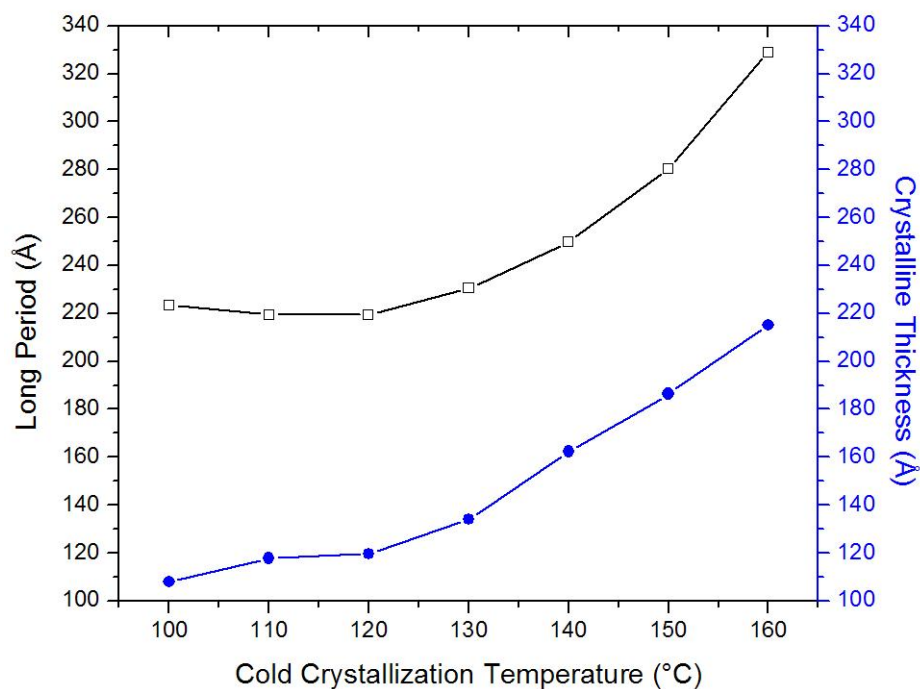


Figure 4.12 Long Period and Crystalline Thickness as a Function of Cold Crystallization Temperature of Cold-crystallized PLLAs

4.2.2 Samples crystallized at 80°C for different period of time

The appearance of the DSC thermograms of PLLA films treated for different period of time at $T_{cc}=80^{\circ}\text{C}$, as shown in **Figure 4.13**. A T_{cII} is observed just prior to the final melting, which presents close similarity to the samples treated at 70°C by Ohtani et al.¹²³. Samples treated for less than 90 minutes are not completely crystallized, resulting in a broad cold-crystallization peak, T_{cI} , in the subsequent heating scan. The longer the annealing time at 80°C is, the smaller the ΔH_{cI} , as expected. When treated for longer than 90 minutes, T_{cI} disappears due to the completion of crystallization, T_{cII} , however, still appears consistently. The quantitative values that can be obtained from the DSC scans in **Figure 4.13** are

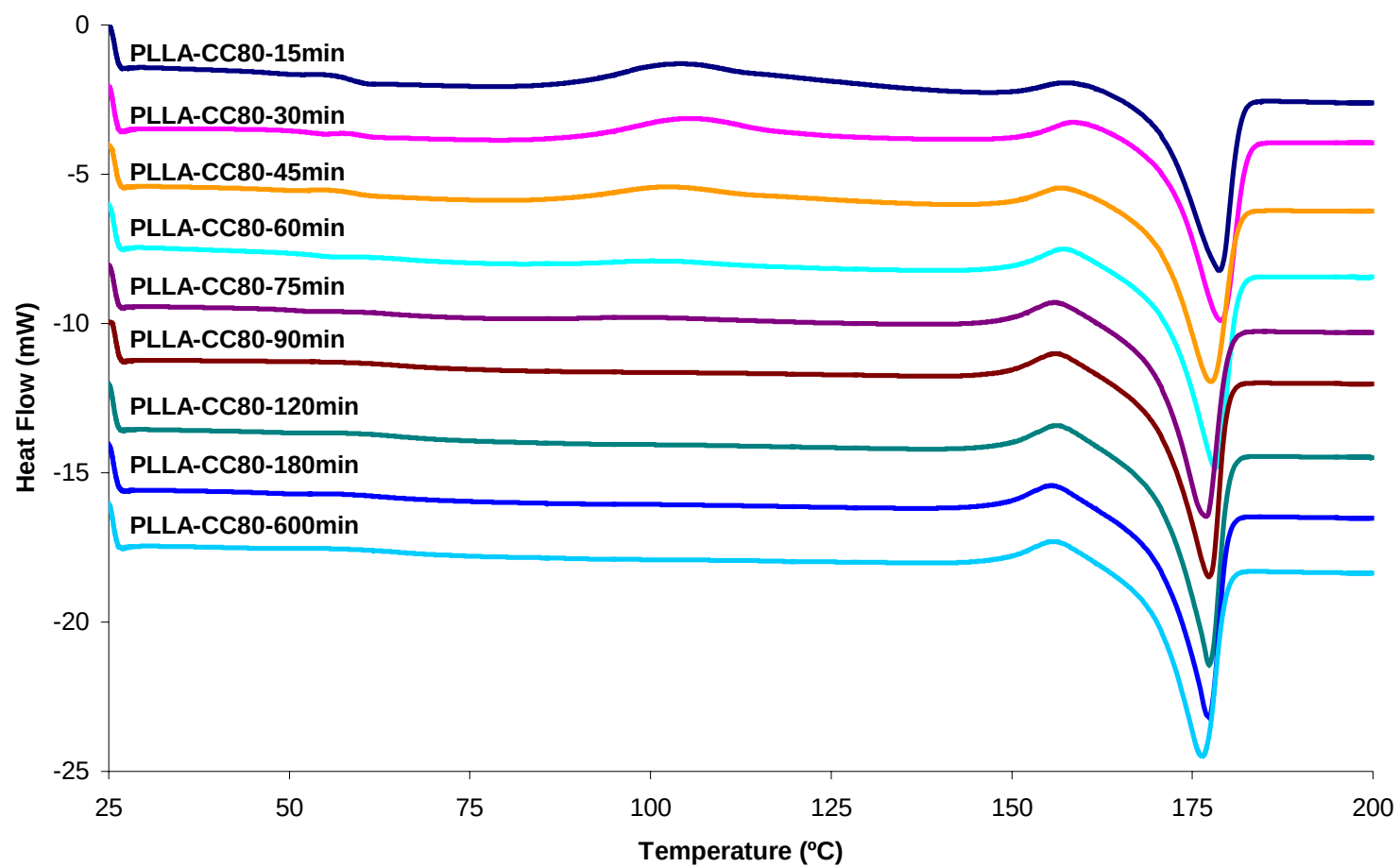


Figure 4.13 DSC Thermograms of PLLA Cold-crystallized at 80°C for Different Period of Time, 10°C/min

presented in **Table 4.3**. The WAXD patterns, **Figure 4.14**, also show a gradual increase of crystallinity with annealing time, consistent with the DSC results in **Table 4.3**. WAXD patterns remain virtually the same when $t_{cc} > 75$ min, as the crystallinity levels off. The two major peaks develop with crystallization time up to around 60 minutes and then remains the same when treatment time prolongs, so does the minor peak located at $2\theta = 24.5^\circ$, which we temporarily associate with so-called δ -crystal.

SAXS of these samples (**Figure 4.15**) does not show any maxima, indicating no periodic arrangement of the crystals even after the sample is treated for 600 minutes, regardless of the strong scattering signals. However, the relative intensity of the scattering does increase with t_{cc} , as a result of the increase in crystallinity. It seems cold-crystallization at 80°C does not develop a long period or yield perfect crystals, no matter how long it is treated or whether the crystallization is completed.

It is also interesting that T_{cI} , T_{cII} and T_{mII} all decrease very slightly with annealing time. In fact, during the annealing at lower temperatures, samples are

Table 4.3 Summary of Observed Thermal Effects of PLLA Cold-crystallized at 80°C for Different Period of Time ($^\circ\text{C}$) and the Degree of Crystallinity

	T_{cI}	T_{mI}	T_{cII}	T_{mII}	$X_{c,h}(\%)$
PLLA-CC80-15min	104.62	-	157.75	178.29	10.4%
PLLA-CC80-30min	105.13	-	158.61	178.47	21.1%
PLLA-CC80-45min	102.62	-	156.94	177.14	24.8%
PLLA-CC80-60min	100.93	-	157.10	176.76	33.9%
PLLA-CC80-75min	99.10	-	156.11	176.61	36.5%
PLLA-CC80-90min	-	-	156.12	176.94	40.4%
PLLA-CC80-120min	-	-	156.27	176.90	42.2%
PLLA-CC80-180min	-	-	155.44	176.91	39.4%
PLLA-CC80-600min	-	-	155.78	175.95	38.5%

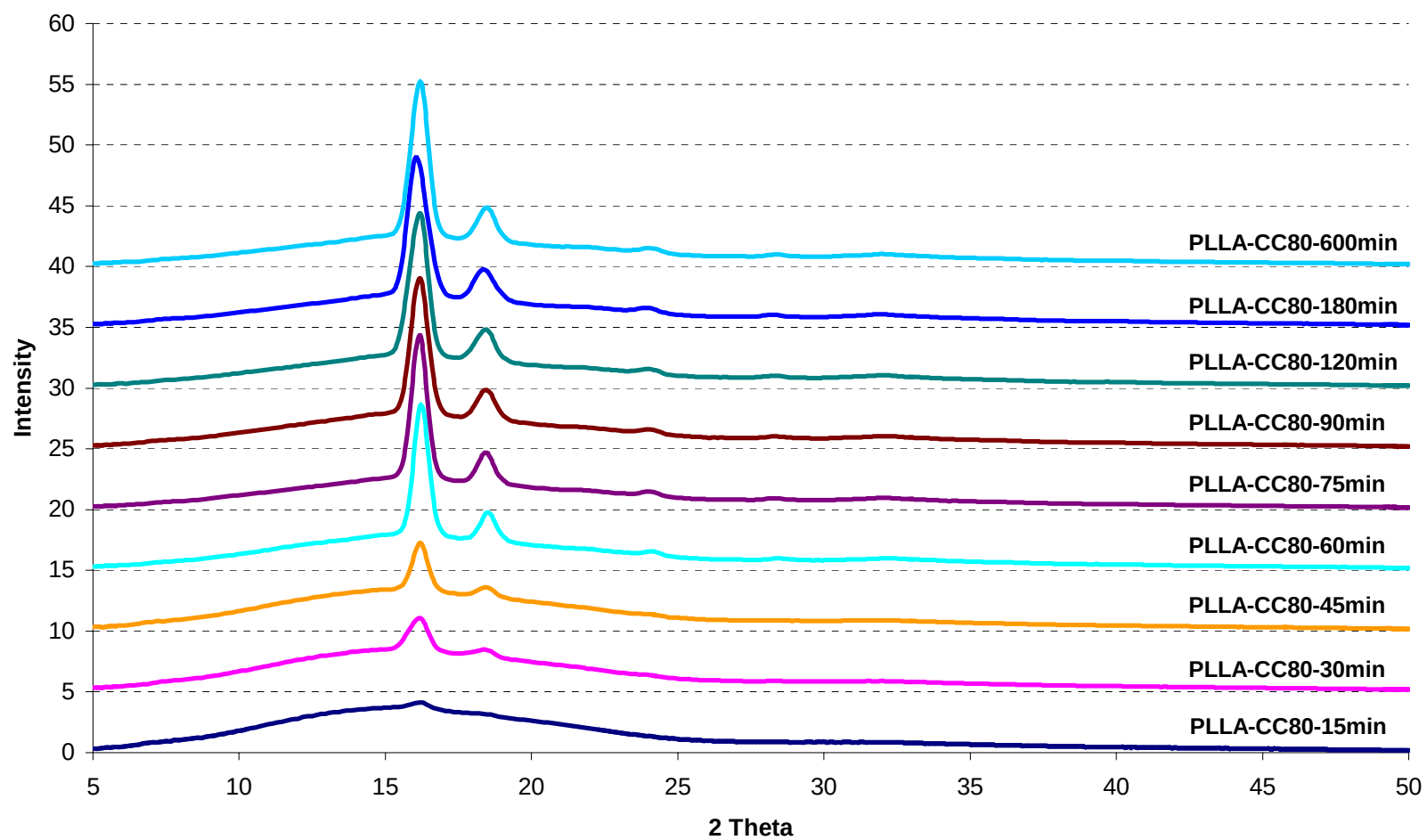


Figure 4.14 WAXD Patterns of PLLA Cold-crystallized at 80°C for Different Period of Time

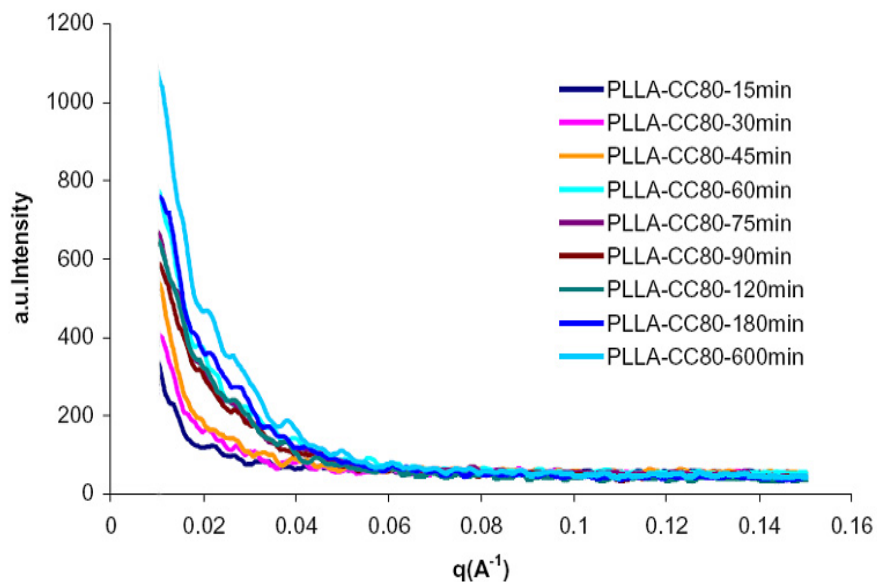


Figure 4.15 SAXS Patterns of PLLA Cold-crystallized at 80°C for Different Period of Time

partially crystallized. These crystals then act as nucleus in the subsequent scans. When annealing time increases, more of such crystals would form, which speeds up the crystallization kinetics, leading to the decrease of crystallization temperature, T_{cI} . With the lowering of T_{cI} , crystallites of less stability can be expected and T_{cII} and T_{mII} decrease accordingly.

It is, so far, clear that temperature is a much more crucial factor to crystallization than time. Further investigation of samples cold-crystallized at 90°C or 100°C show qualitatively similar DSC profile with increase in t_{cc} . It is not until T_{cc} reaches the neighborhood of 108°C that qualitative changes of appearance can be observed on subsequent DSC scans within the t_{cc} range studied (**Figure 4.16**). When treated at $T_{cc}=110^{\circ}\text{C}$ at 60, 240, and 600 minutes, the DSC thermograms in **Figure 4.17** again show consistency with the assumption of melt-recrystallization, i.e. as t_{cc}

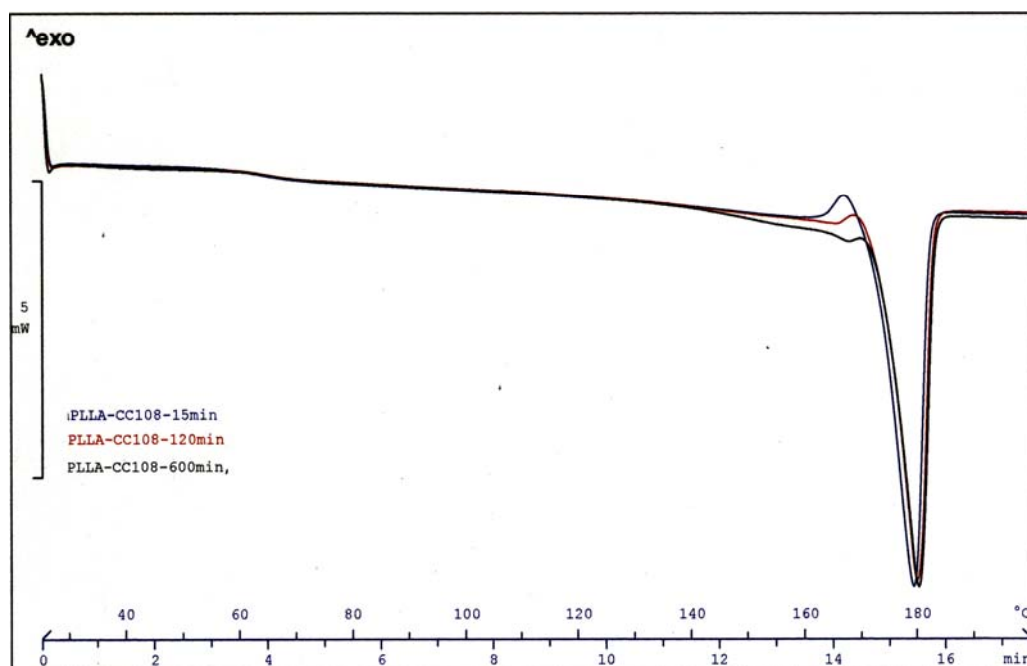


Figure 4.16 DSC Thermograms of PLLA Cold-crystallized at 108°C for 15, 120 and 600 minutes

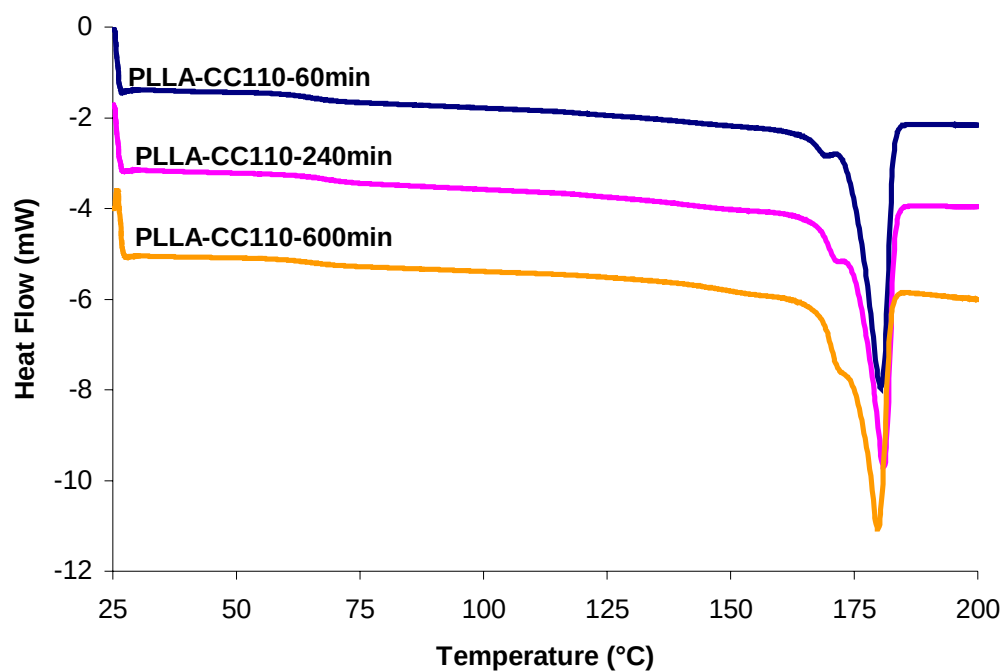


Figure 4.17 DSC Thermograms of PLLA Cold-crystallized at 110°C for 60, 240 and 600 minutes

increases, ΔH_{mI} increases while ΔH_{mII} decreases, although the changes in T_{mI} and T_{mII} are marginal. Obviously, crystals formed at longer treatment time are more stable, resulting in less recrystallization during the heating which encourages the melting of more original crystals and less reorganized crystals during the DSC scan.

4.2.3 Heating rate effect on samples crystallized at 100°C and 120°C for 1 hr

Heating rate effect is a common measurement to test the existence of melt-recrystallization phenomena. According to the melt-recrystallization mechanism, it can be expected that ΔH_{mI} increases and T_{mI} shifts to a higher temperature, while ΔH_{mII} decreases and T_{mII} shifts to a lower temperature with the increasing heating rate, provided T_{mI} is associated with the originally formed crystal and T_{mII} is due to the melt-recrystallization. This is due to constraint imposed on reorganization process. Ideally, T_{mII} would completely vanish at certain heating rate when recrystallization is totally inhibited.

The effect of heating rate on double melting behavior was studied on PLLA-CC100-60min samples at heating rate 2.5, 5, 10, 20, 30, 40, and 50°C/min. All the DSC thermograms are normalized and shifted for better presentation, as illustrated in **Figure 4.18**. **Figure 4.19** displays selected individual scans so as to give a more distinctive exhibition of the changes that occurred with the rising heating rate, which could not be seen clearly in **Figure 4.18** due to the scale factor. As seen in **Figure 4.19**, as the heating rate increases, ΔH_{mI} increases very slowly yet noticeably, although T_{mI} itself is difficult to determine at lower heating rates. T_{cII} increases

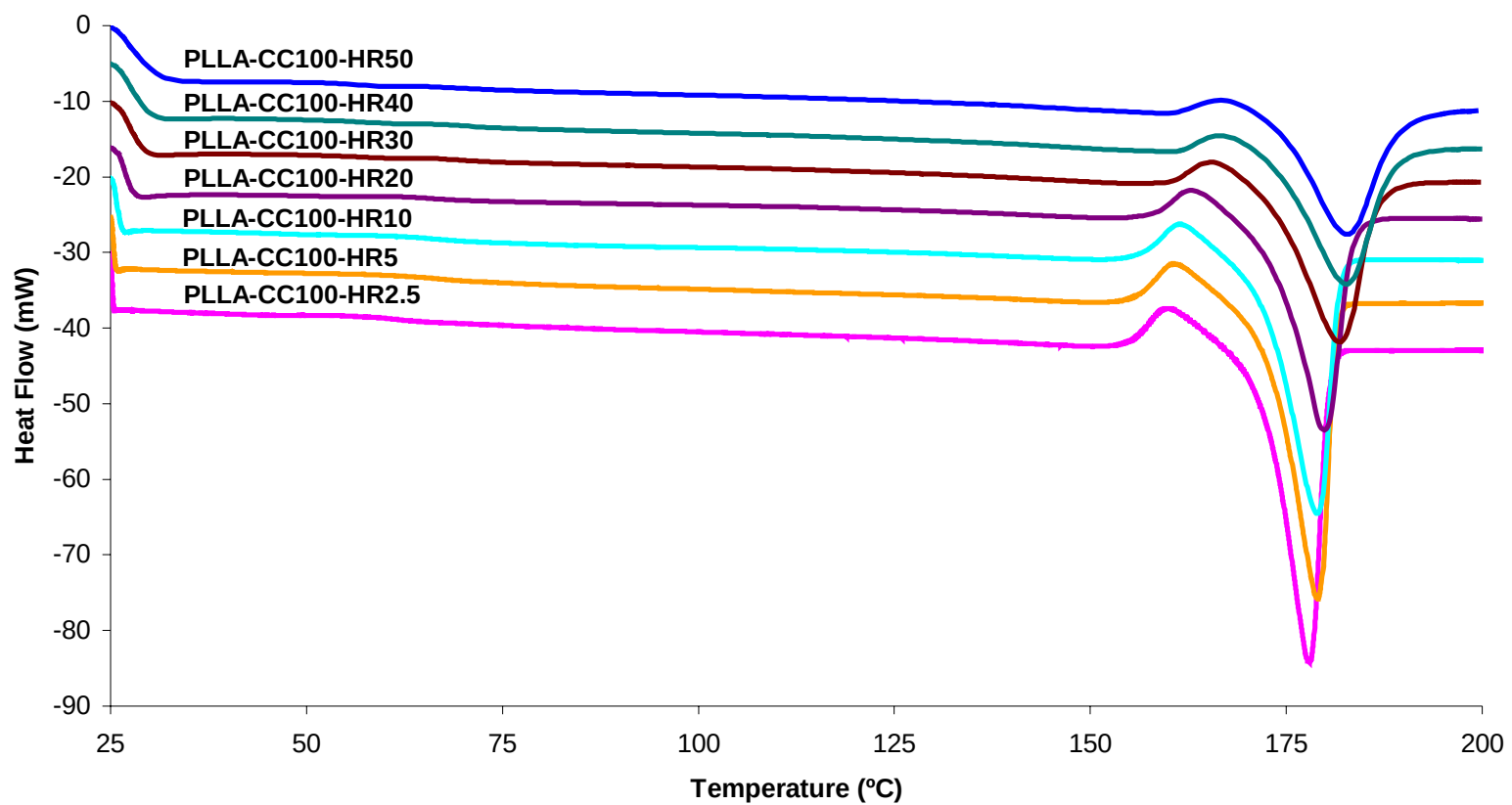


Figure 4.18 DSC Thermograms of PLLA-CC100-60min Scanned at Different Heating Rate

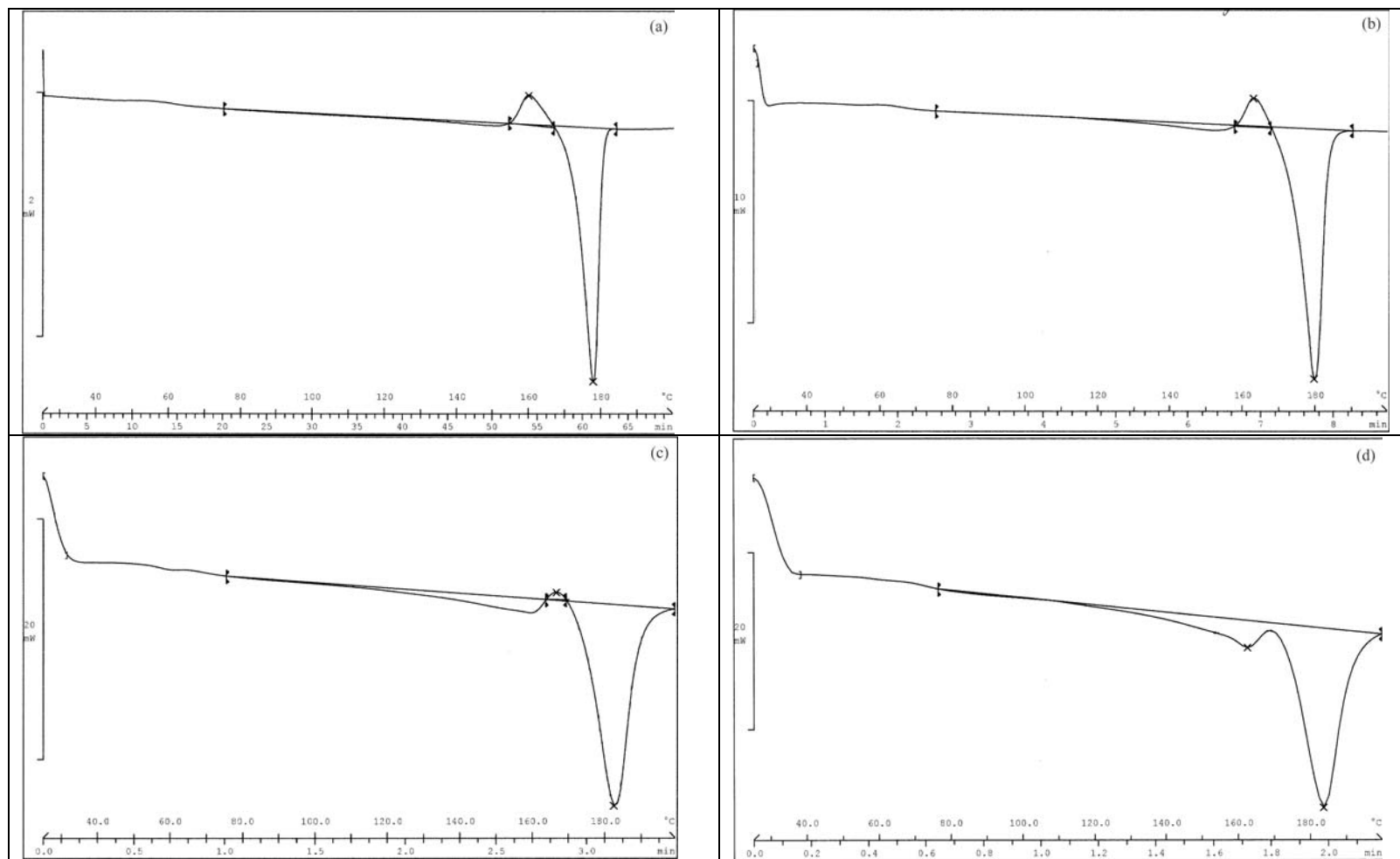


Figure 4.19 Selected Individual DSC Thermograms of PLLA-CC100-60min Subject to (a) 2.5°C/min, (b) 20°C/min, (c) 50°C/min, and (d) 80°C/min Heating Rate

gradually up to the heating rate of 30°C/min, and then tends to level off, while ΔH_cII decreases slightly from about -7.5 J/g to -0.5J/g with the rising heating rate up to 50°C/min. Both observations from T_mI and T_cII seem to be consistent with the suggestion of melt-recrystallization mechanism. As heating rate increases, there is less time for the samples to recrystallize, causing ΔH_mI to increase, T_cII to occur at a higher temperature, and ΔH_mII to decrease. T_mII , however, took the opposite direction to that expected. Instead of decreasing with increasing heating rate, it increases very gradually (within 3°C). This is not altogether surprising though considering the effect of superheating at elevated heating rate. When the projected decrease of T_mII is relatively small, its net effect with superheating could easily overturn the trend we anticipated.

It is expected that continuous increase of heating rate will eventually completely inhibit the recrystallization, leading to only one melting peak. However, at heating rate as high as 80°C/min, double melting still exists, as shown in **Figure 4.18(d)**, which suggests that the recrystallization of PLLA needs very low energy to initiate and it starts almost instantaneously whenever imperfect crystals exists. Also the rate of melting and that of recrystallization are still competitive at such a high heating rate.

The heating rate effect is more evident in PLLA-CC120-60min samples, as shown in **Figure 4.20**. At heating rate lower than 10°C/min, distinctive double-melting phenomena are observed. Individual DSC thermograms of lower heating rate scans are revealed in **Figure 4.21**. At heating rate 1°C/min, ΔH_mII is more prominent

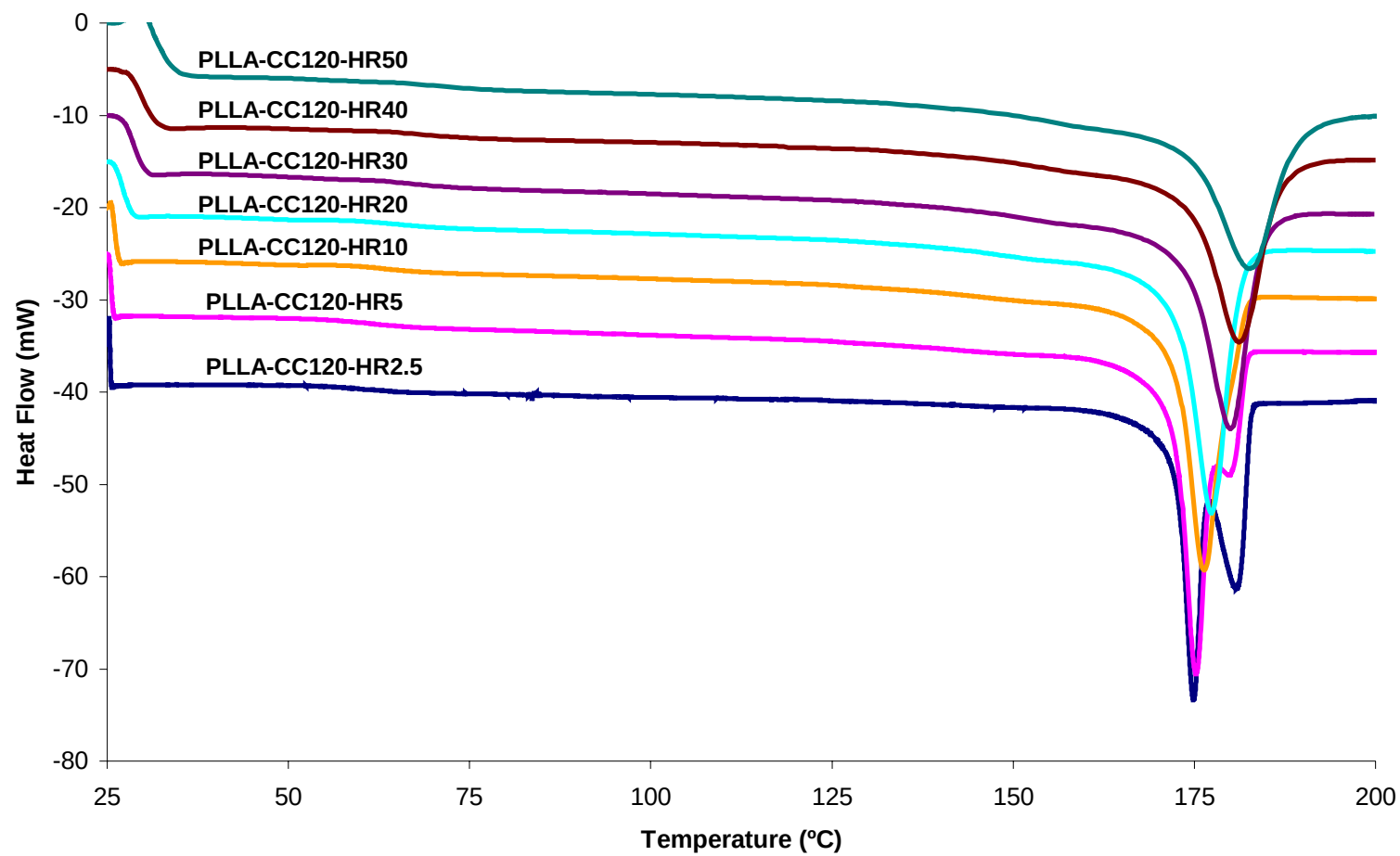


Figure 4.20 DSC Thermograms of PLLA-CC120-60min Scanned at Different Heating Rate

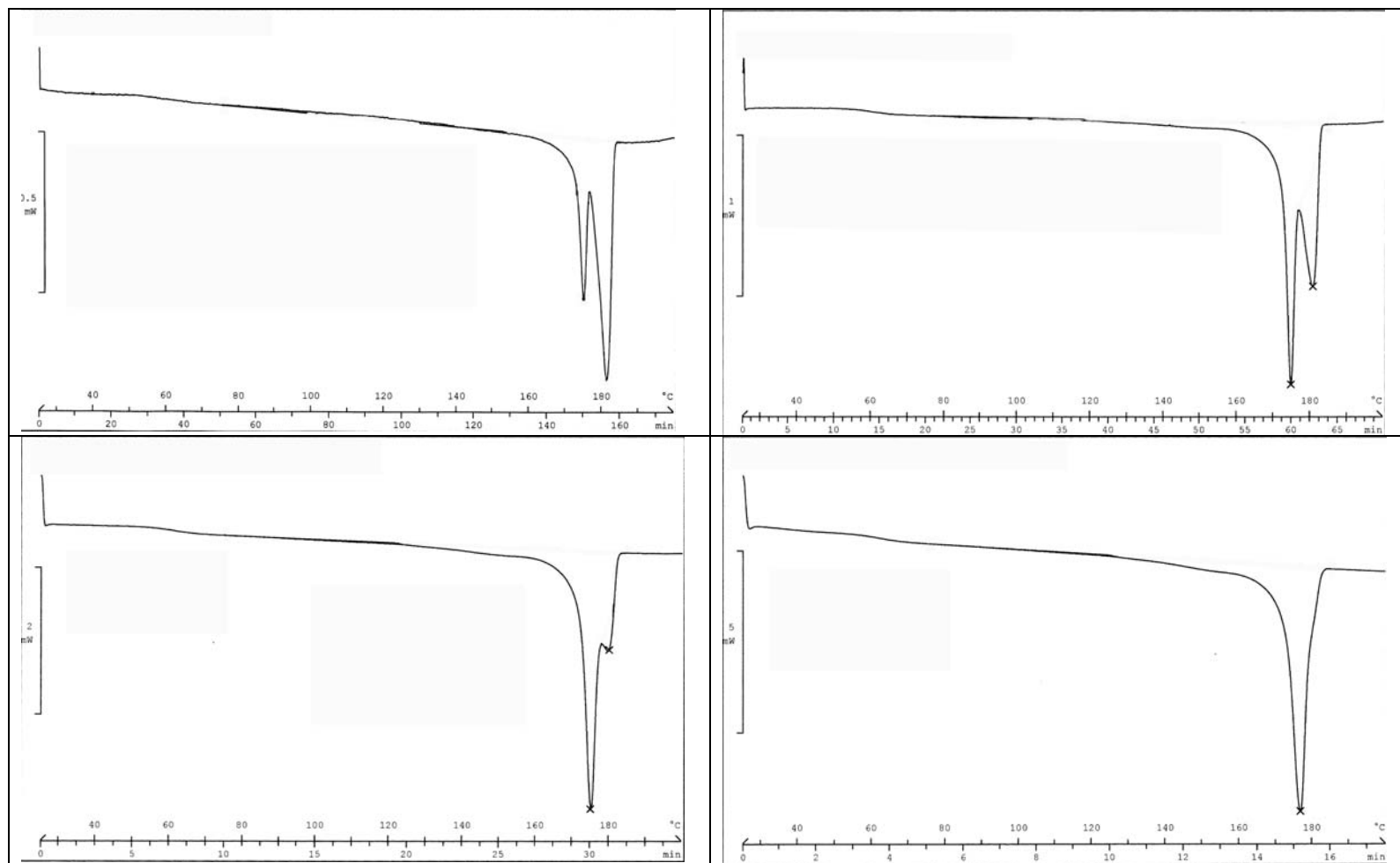


Figure 4.21 Selected Individual DSC Thermograms of PLLA-CC120-60min Subject to (a) 1°C/min, (b) 2.5°C/min, (c) 5°C/min, and (d) 10°C/min Heating Rate

than ΔH_{mI} . As heating rate increases to 2.5°C , ΔH_{mI} becomes larger than ΔH_{mII} . Further increase of heating rate to 5°C results in the domination of ΔH_{mI} over ΔH_{mII} . Moreover, during the process of rising heating rate, T_{mI} gradually increases while T_{mII} decreases; though the extent is very slight, which seems to be characteristic to this PLLA. Eventually, when heating rate turns to $10^{\circ}\text{C}/\text{min}$, only ΔH_{mI} is observable. When heating rate exceeds $10^{\circ}\text{C}/\text{min}$, only one peak is present, and the peak temperature gradually increases as superheating becomes more and more severe with increasing heating rate. Therefore, $T_{mI}=175.97^{\circ}\text{C}$ is the closest approximation of the actual T_{mI} of the original crystals formed at 120°C after 1 hr treatment. In principle, the actual T_{mI} of a sample can be determined by changing heating rate until a single peak first appears free of superheating.

All the above observations fit the description of the alleged melt-recrystallization mechanism. It is noteworthy that double melting peaks finally merge to a single peak when heating rate is $10^{\circ}\text{C}/\text{min}$. Looking back on the case of PLLA-CC100-60min, we believe that the reorganization process is so fast when tremendous amount of small imperfect crystals are formed under that condition that even when heating rate reaches $80^{\circ}\text{C}/\text{min}$, the driving force of recrystallization is so high that it still could not be prevented.

4.2.4 Molecular weight effects on the double melting of PLLA

In addition to what is already covered, the molecular weight effect on the double melting behavior was also studied. Samples were prepared by holding the

original PLLA film at 210°C for different periods of time before quenching to ice-water mixture. The molecular weights were then determined by GPC.

The molecular weight effect on multiple melting behavior has been studied on different polymers, such as PEEK⁵⁷, PET⁹³, iPP^{145, 146} and PBS¹⁴⁷. Fournies et al.⁵⁷ suggested that the reorganization of the lamellae is strongly hindered for high molecular weight samples due to the presence of chain entanglements that lower the rate of recrystallization considerably. Medellin-Rojdriguez et al.⁹³, on the other hand, believe that the higher entanglement density that results from an increase of molecular weight increases the fraction of initially rejected chain sections and therefore the amount of secondary crystallization. So that the second melting endotherm increased at the expense of the third one as the average molecular weight was increased. Jamshidi et al.⁴⁰ observed weak double melting peaks for PLLAs with molecular weights lower than 3,000. They suggested that those broad T_mI peaks be attributed to the unstable crystallized region and disappears with increasing molecular weight.

As shown in **Figure 4.22**, although considerable original mass (72%) was retained after 240 minutes holding time at 210°C, according to TGA, the molecular weights deteriorate much faster. After 60 minutes, the original molecular weight is reduced by about 80%. The degraded samples of various extents were then scanned in the DSC from 25°C to 200°C with 10°C/min, as demonstrated in the thermograms in **Figure 4.23**. All the samples were initially amorphous, showing net crystallinity close to 0%. T_g continues to drop as the molecular weight decreases, as tabulated in **Table 4.4**. Meanwhile, T_cI decreases and becomes narrower as shortened molecular chains facilitate the cold-crystallization. Double melting behavior is not so obvious when

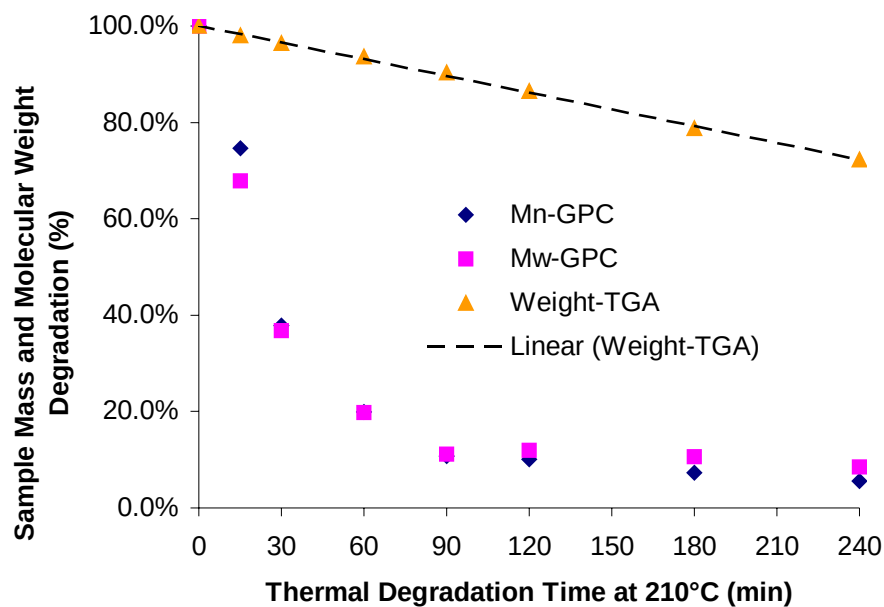


Figure 4.22 Molecular Weight (GPC) and Mass (TGA) Changes for PLLA Held at 210°C for Different Period of Time

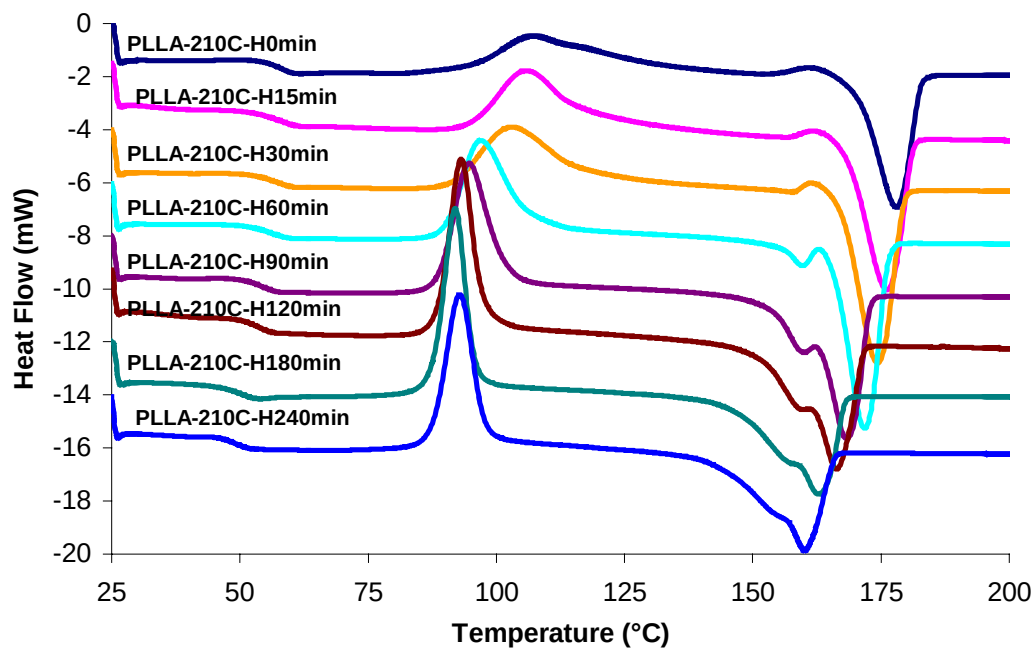


Figure 4.23 DSC Thermograms of PLLA with Different Molecular Weights

Table 4.4 Glass Transition, Cold-crystallization and Melting Temperatures of PLLA Amorphous Samples with Different Molecular Weights

	M_n (g/mol)	T_g (°C)	T_{cI} (°C)	T_{mI} (°C)	T_{cII} (°C)	T_{mII} (°C)
PLLA-H0min	156k	57.64	107.32	-	160.93	177.68
PLLA-H15min	116k	56.41	105.99	-	161.55	175.78
PLLA-H30min	59k	56.25	103.00	157.73	161.18	173.93
PLLA-H60min	31k	55.43	97.06	159.36	-	171.41
PLLA-H90min	17k	53.89	94.76	159.64	-	167.99
PLLA-H120min	16k	52.99	93.31	159.10	-	166.00
PLLA-H180min	11k	49.65	92.71	156.80	-	162.58
PLLA-H240min	9k	48.65	92.96	154.64	-	159.91

molecular weight is still high. T_{cII} is still showing if the sample has only been degraded for 30 minutes or less, which, as we already established, is due to the close competition between melting and recrystallization, as well as the low quality of the crystals formed. When degraded at longer times, double melting becomes more obvious and the ratio between ΔH_{mI} and ΔH_{mII} increases with it. At the same time, the melting peaks, T_{mI} and T_{mII} , gradually decrease and broaden. High molecular weight PLLA, which has longer chain length, would contain more chain entanglements upon quenching. When heated up subsequently at the same rate 10°C/min, the limited chain mobility of higher molecular weight PLLA would crystallize to relatively less perfect crystals even at a higher T_{cI} . These crystals would have a stronger tendency to go through reorganization. However, the rate of both melting and recrystallization is highly restricted by the chain mobility as well. Thus, the double melting is actually not easily recognized until M_n drops to the neighborhood of 30,000.

4.2.5 Partial melting of samples crystallized at 100°C for 1 hr

The DSC thermogram of PLLA cold-crystallized at 100°C for 60 minutes (PLLA-CC100-60min) shows T_{mI} (very slightly), T_cII and T_{mII} , as in **Figure 3.4**, thus is a good condition to study the partial melting behavior of PLLA in order to help understand the origin of double-melting in PLLAs. Different temperatures are chosen to perform the partial melting, which are indicated in **Figure 3.4**.

Figure 4.24 shows the overall DSC thermograms of PLLA-CC100-60min after partial melting at different temperatures. After partial melting in the range 120 – 155°C, T_cII still exists in the subsequent DSC scans, with T_{mI} as a small but broad peak underneath the baseline, showing that the continuous recrystallization still persists from where it was interrupted. When partially-melted at 160°C, i.e. almost at the peak of the recrystallization peak (see **Figure 3.4**), double melting peak becomes obvious, again indicating reorganization process. Beyond 160°C, the subsequent DSC thermogram only shows one sharp peak. As 165°C is near the end of T_cII or the melt-recrystallization, the crystals are close to perfection, and that is probably why only a small shoulder was shown prior to the melting. T_{mII} remains constant for samples that partially crystallized below 165°C, as shown in **Table 4.5**, indicating the perfection of crystals formed under these partial melting conditions are virtually the same. When partially melted at more elevated temperature, no recrystallization exists, but crystals thicken, resulting in a bit higher melting temperatures.

The thermograms of PLLA-CC100-p120C, PLLA-CC100-p130C, and PLLA-CC100-p140C are similar, so are their WAXD patterns, as demonstrated in

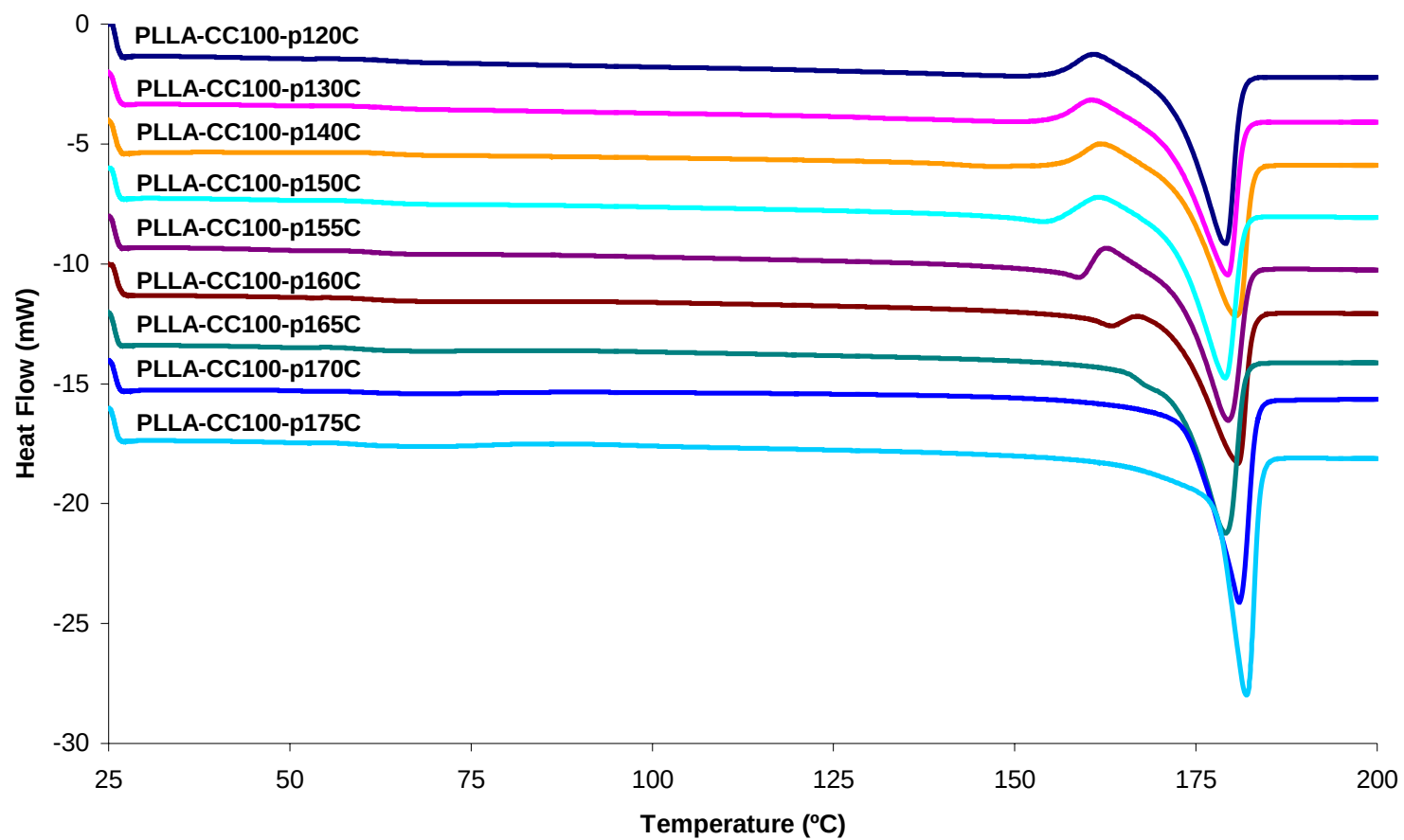


Figure 4.24 DSC Thermograms of PLLA-CC100-60min Partially-Melted at Different Temperature

Table 4.5 Summary of Observed Thermal Effects PLLA-CC100-60min Partially Crystallized at Different Temperature (°C) and the Degree of Crystallinity

	T_{cI}	T_{mI}	T_{cII}	T_{mII}	X_{ch} (%)
PLLA-CC100-p120C	-	trace	160.94	178.58	49.4%
PLLA-CC100-p130C	-	trace	160.62	178.94	49.3%
PLLA-CC100-p140C	-	trace	161.44	178.59	48.9%
PLLA-CC100-p150C	-	154.38	161.45	178.60	49.9%
PLLA-CC100-p155C	-	158.69	162.61	179.11	49.1%
PLLA-CC100-p160C	-	164.40	-	178.44	54.0%
PLLA-CC100-p165C	-	shoulder	-	178.74	55.9%
PLLA-CC100-p170C	-	-	-	180.04	57.2%
PLLA-CC100-p175C	-	-	-	181.44	59.2%

Figure 4.25. From the shape of T_{mI} and T_{cII} , it seems that recrystallization occurs almost at the same temperature range, while T_{mI} increases with the partial melting temperature, about 4°C higher than T_{pm} . It indicates the gradual improvement of perfection of the crystals formed at that particular temperature during the heating scan of PLLA-CC100-60min. From both WAXD patterns in **Figure 4.25** and DSC results listed in **Table 4.4**, the crystallinity increases when partial melting goes through the exothermic peak T_{cII} , which is a quite typical observation for materials that experience melt-recrystallization during the heating. It is also interesting to see that the peak at $2\theta=24.5^\circ\text{C}$, or the δ -phase, persistently exists in all the partially-melted samples even when at 175°C . This further assures that no transition from δ -phase to α -phase takes place over the recrystallization, T_{cII} , region.

The Lorentz corrected SAXS pattern (**Figure 4.26**) shows that the scattered intensity first increases gradually without much change in the long period. Beyond 155°C (**Table 4.6**, **Figure 4.27**), the long period rises much more rapidly and so does

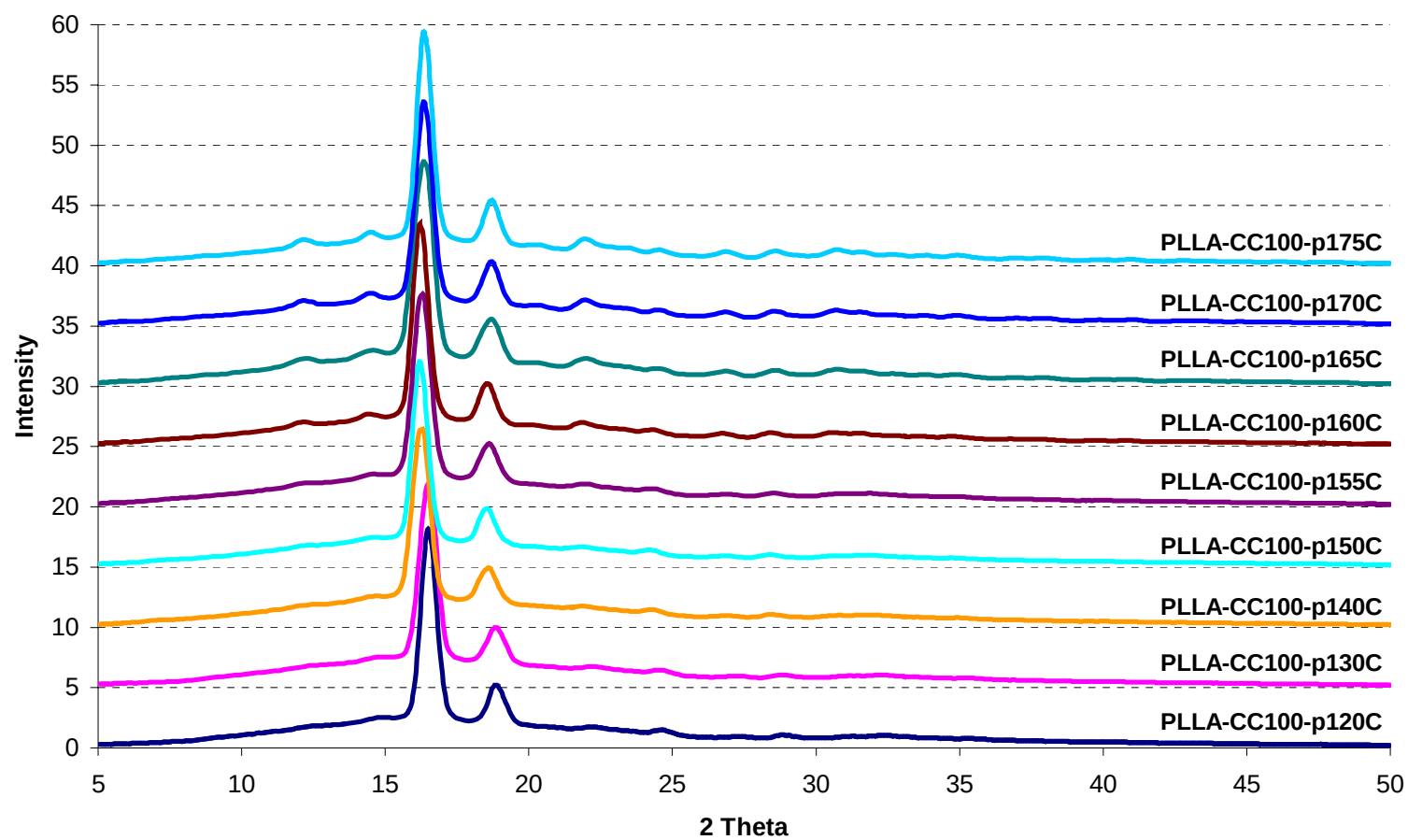


Figure 4.25 WAXD Patterns of PLLA-CC100-60min Partially-Melted at Different Temperatures

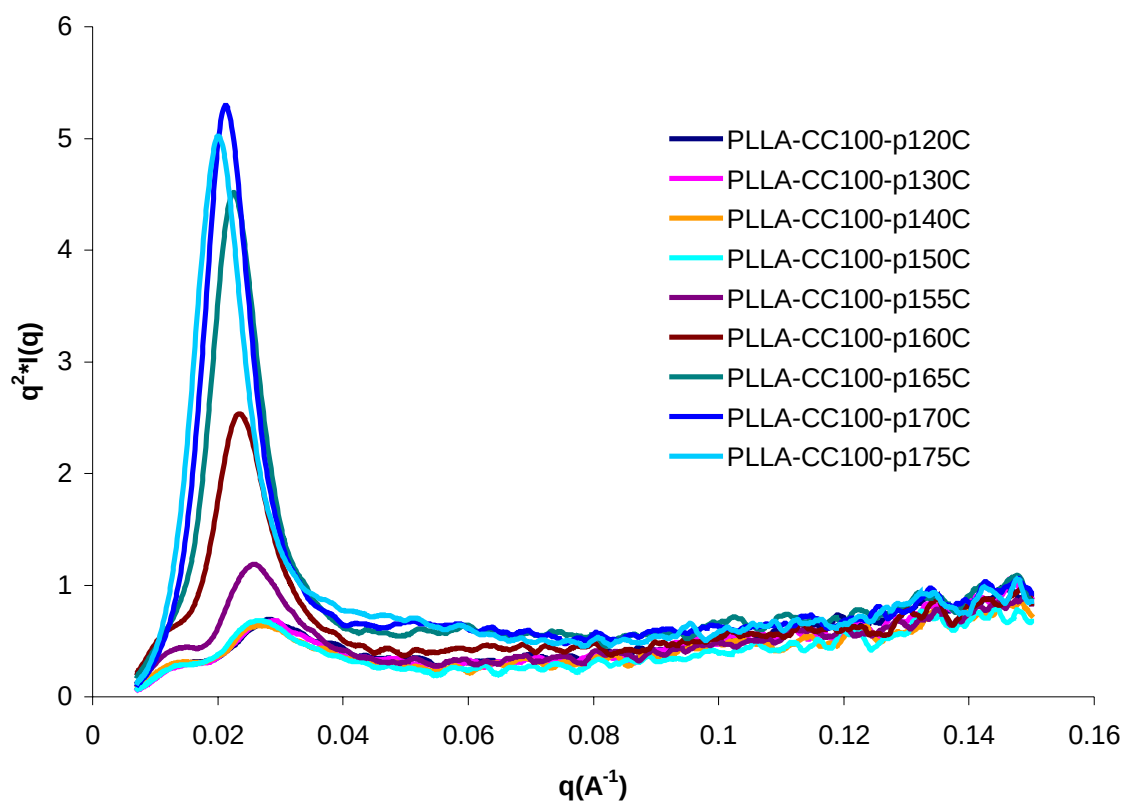


Figure 4.26 Lorentz Corrected SAXS of PLLA-CC100-60min Partially Melted at Different Temperatures

Table 4.6 Long Period and Lamellar Thickness of PLLA-CC100-60min Partially Melted at Different Temperatures

	$q_{\max}$ ($\text{\AA}^{-1}$)	$L_{\max}$ ($\text{\AA}$)	l_c ($\text{\AA}$)
PLLA-CC100-p120C	0.028131	223.35	110.31
PLLA-CC100-p130C	0.027491	228.55	112.75
PLLA-CC100-p140C	0.026909	233.50	114.18
PLLA-CC100-p150C	0.026392	238.07	118.68
PLLA-CC100-p155C	0.025697	244.51	119.96
PLLA-CC100-p160C	0.023437	268.09	144.79
PLLA-CC100-p165C	0.022569	278.40	155.57
PLLA-CC100-p170C	0.021180	296.66	169.60
PLLA-CC100-p175C	0.020139	311.99	184.54

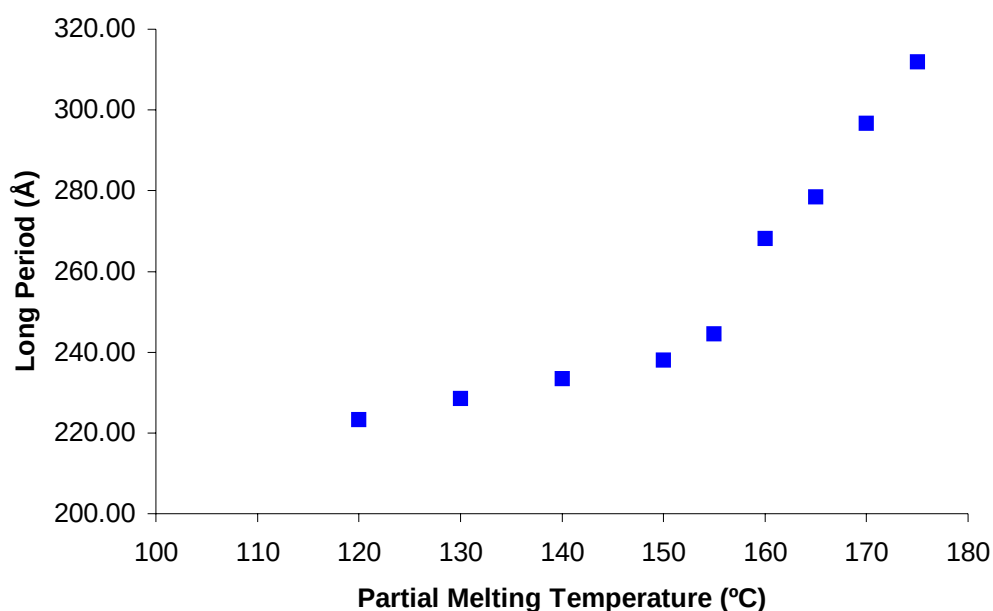


Figure 4.27 Lamellar Long Period as a function of Partial Melting Temperatures of PLLA-CC100-60min

the lamellar thickness. Hsiao et al.⁶⁴, who observed similar trend in PEEK, believed it is a sign of two different lamellar thickness. However, that could not have explained the existence of the exotherm between the two melting endotherms. We believe that below 155°C, the reorganization is in the form of gradual yet continuous crystal perfection due to the close competition of melting and recrystallization. Then from 155°C to 165°C, recrystallization overwhelms melting; giving reorganization a big boost and the long period shows substantial increase. Then the lamellae thicken at even higher temperature before it eventually melts.

4.3 SUMMARY

Melting behavior of poly(L-lactic acid) film crystallized from glassy state, either isothermally or non-isothermally, was studied by DSC, TMDSC, WAXD, and SAXS. Double cold-crystallization peak of amorphous PLLA film occurs when melt-recrystallization initiates before cold-crystallization of the metastable crystals even finishes, and its extent is strong enough to compete with cold-crystallization at heating rate 10°C/min. The overall appearance of the curve represents the combination of cold-crystallization during the heating, and the instant melting and recrystallization of these unstable crystals.

T_{mI} of the double melting peak, mostly masked by an exothermic peak, T_{cII} , before final melting. This gives the appearance of only $T_{cII}+T_{mII}$, instead of being two obvious endotherms $T_{mI}+T_{mII}$. This result is due to the close competition between melting and recrystallization. The occurrence of double melting is a function of crystallization temperature, crystallization time, heating rate, and molecular weight. It occurs in samples isothermally cold-crystallized below 120°C, even when the crystallization is essentially completed in 60 minutes above 80°C, and the resultant crystallinity reaches as high as about 50%. This is due to the formation of a large amount of small and imperfect crystals at lower crystallization temperature, which do not even form periodic lamellar structure.

Temperature is proven to be a more significant factor than time with regard to improving crystal perfection and removal of double melting. Both heating rate and partial melting tests confirmed the mechanism of melt-recrystallization being the

cause of double melting for samples cold-crystallized below 140°C. For samples cold-crystallized above 140°C, the appearance of double melting is due to the existence of a dual lamellar population.

Although multiple evidences support the melt-recrystallization theory, we still hold the reservation that it might not be the sole mechanism responsible for the double melting of amorphous PLLA films. A possible δ -phase, which may have mixed with α -phase, could also contribute to the double melting as have been suggested similarly by Ohtani et al.¹²³, although from our observation, the transformation from δ -phase to α -phase at elevated temperature seems unlikely.

At the same heating rate, the double melting behavior is not as prominent for high molecular weight PLLA as for lower ones, due mainly to the larger amount of entanglements that existed in the amorphous state that restrain the chain mobility, which consequently slows the rate of both melting and recrystallization.

CHAPTER 5 SAMPLES CRYSTALLIZED FROM THE MELT

5.1 NON-ISOTHERMAL CRYSTALLIZATION FROM THE MELT

5.1.1 Samples crystallized at different cooling rate

The DSC thermograms of dynamic cooling of PLLA melt at different rates, from $-0.5^{\circ}\text{C}/\text{min}$ to $-20^{\circ}\text{C}/\text{min}$, to room temperature are shown in **Figure 5.1**. Each curve is normalized according to the heating rate and then shifted for better presentation. The curves of PLLA-CR0.5 and PLLA-CR1 are not as smooth as the rest of the curves due to the limitation of sensitivity of the equipment at such low cooling rates. In each DSC curve exhibiting crystallization, only a single exothermic crystallization peak, T_c , appears, which suggests a single crystallization process during the dynamic cooling procedure. Therefore, the distribution of the crystallites size in such a melt-crystallized sample is believed to be unimodal instead of bimodal. Consequently, the occurrence of double melting peaks during the subsequent heating scan should not be associated with the possibility of bimodal size distribution of the crystallites.

As expected, the crystallization temperature decreases with increasing cooling rate; so does the crystallinity calculated from DSC using Fischer's ¹¹⁵ value of 93 J/g for 100% PLLA crystal, both of which are listed in **Table 5.1**. T_c decreases faster at first as the cooling rate increases from PLLA-CR0.5 to PLLA-CR3, and then becomes stable around 102°C when cooling rate is over PLLA-CR4. Meanwhile, the width of the peak also becomes broader and a definite T_g starts to show around 60°C as the cooling rate increases in comparison to the molecular motion. It seems that the growth

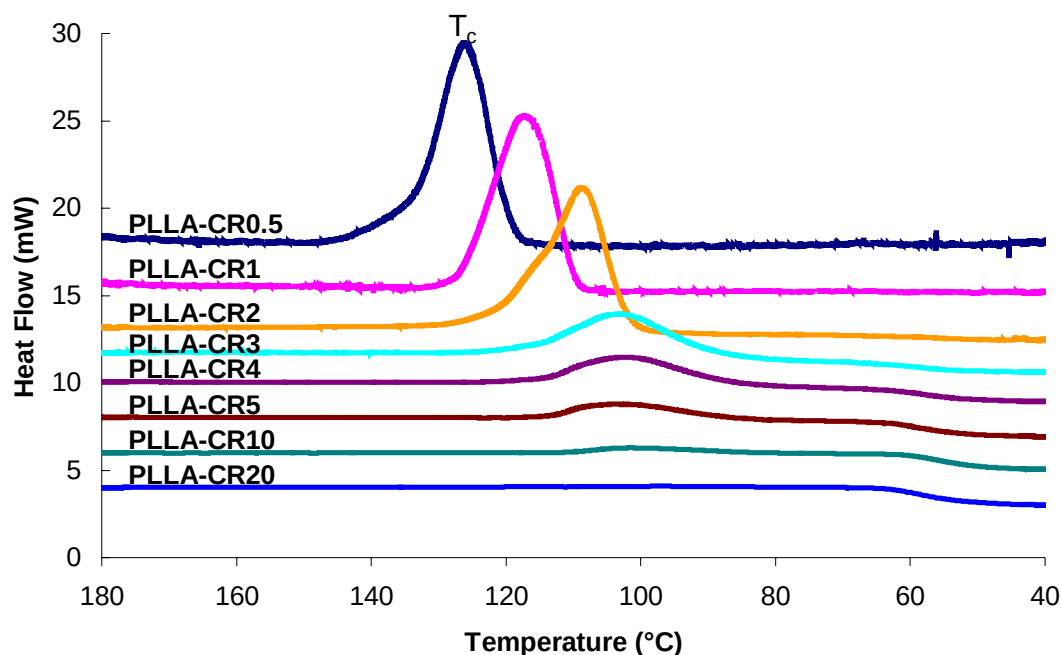


Figure 5.1 DSC Thermograms of Non-isothermal Melt-crystallization of PLLA at Different Cooling Rates

Table 5.1 Crystallization Temperature, Crystallinity, Long Period, Lamellar Thickness of Non-isothermal Melt-crystallized PLLAs from Different Cooling Rates

	T_c (°C)	$X_{c,h}$ (%)	L_{max} (Å)	l_c (Å)	l_a (Å)
PLLA-CR.5	125.68	62.7%	169.88	105.51	63.36
PLLA-CR1	115.62	51.7%	182.75	94.48	88.27
PLLA-CR2	108.03	40.7%	201.02	81.82	119.21
PLLA-CR3	102.80	31.6%	199.91	63.17	135.74
PLLA-CR4	102.24	19.2%	231.95	44.53	187.41
PLLA-CR5	101.96	12.1%	229.01	27.71	201.30
PLLA-CR10	101.83	2.8%	-	-	-
PLLA-CR20	-	0.0%	-	-	-

rate decreases faster than the nucleation rate increases, resulting in an overall decrease of crystallization rate. Consequently, a significant drop in T_c , from 125°C to 102°C was observed as the cooling rate rises. The drop of T_c is accompanied with declining crystallinity values, as well as the generation of smaller and more imperfect crystals in these melt-crystallized samples. As crystallinity continues to drop with increasing cooling rate, it was not until it reached -20°C/min (PLLA-CR20) that the crystallinity becomes zero percent or completely amorphous, which is consistent with the WAXD crystallinity as estimated from the diffraction patterns in **Figure 5.2**. As the cooling rate increases, the intensity of two major peaks, (110)/(200) and (113)/(203), noticeably decreases, while losing details in other minor peaks, such as (103), (011), (211), etc. Eventually, only an amorphous halo is shown when the cooling rate reaches 20°C/min, which is the cooling rate that will be used in isothermal melt-crystallization when the sample is cooled from the melt to the designated crystallization temperature, T_{mc} . It is noteworthy that all WAXD patterns are consistent with the α -crystal modification of PLLA, although the weak peaks fade into the background at higher cooling rate. Also included in **Table 5.1** is the lamellar thickness of these samples calculated from long periods obtained from SAXS measurements and the crystallinity obtained from DSC. As illustrated in **Figure 5.3**, the thickness of crystalline phase decreases while that of amorphous phase increases, both linearly as a function of increasing cooling rate. The SAXS shows no peak for samples melt-crystallized at PLLA-CR10 and PLLA-CR20, but still shows a weak yet detectable peak at PLLA-CR5, which yields 12.1% crystallinity in DSC. As we recall

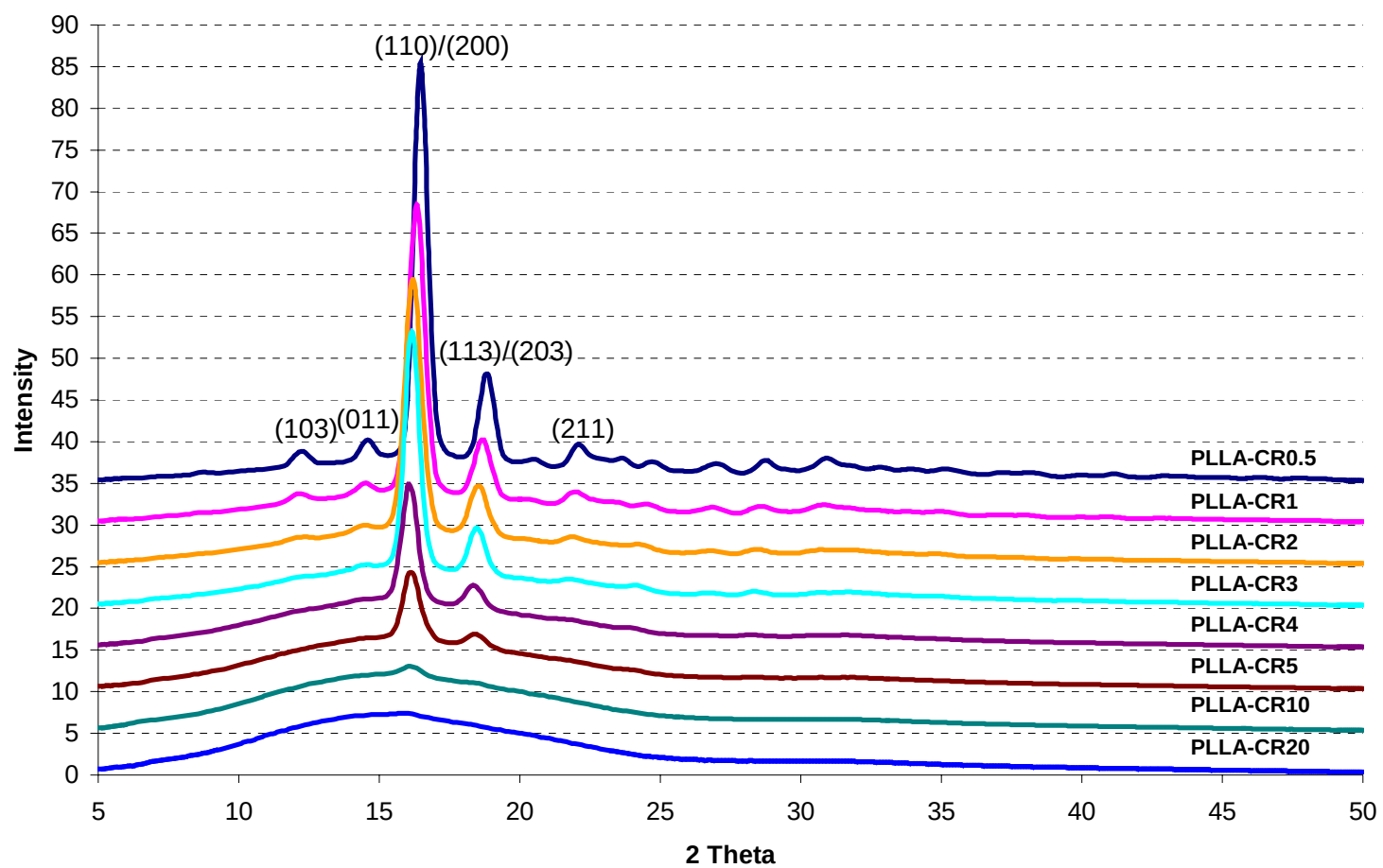


Figure 5.2 WAXD Patterns of Non-isothermally Melt-crystallized PLLA at Different Cooling Rates

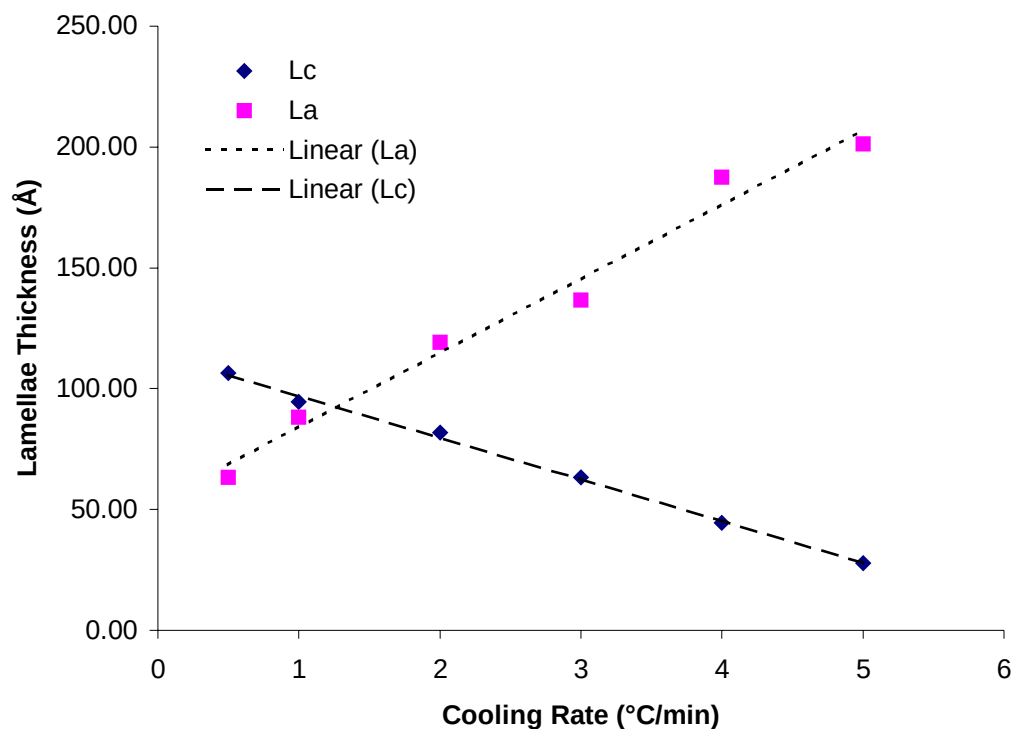


Figure 5.3 Crystalline and Amorphous Thickness of PLLA Melt-crystallized Non-isothermally at Different Cooling Rates

in the previous investigation of cold-crystallized samples, samples cold-crystallized at 80°C, PLLA-CC80-time, no matter how long it is crystallized, or whether the crystallization completed, SAXS shows no periodicity even when crystallinity reaches as high as 40% and the scattering is strong. According to T_c , most of the PLLA-CR samples are crystallized above 100°C, which gives rather perfect crystals that forms lamellae structure regardless of limited crystallinity.

5.1.2 Heating rate effect on double melting of non-isothermally crystallized samples

After non-isothermal melt-crystallization at different dynamic cooling rate, samples are heated up again to 200°C at different heating rate to examine the appearance of double melting phenomena. It is noticed that within all the scans, only a few of them showed distinctive double melting peaks, $T_{mI}+T_{mII}$, which is indicated as “✓” in **Table 5.2**. Most of incidences do not show very obvious double melting phenomena. Instead, an exothermic peak, T_{cII} , is shown just prior to the final melting T_{mII} , $T_{cII}+T_{mII}$ (T_{mI} does not show because recrystallization overwhelms melting). This condition is marked as “X” in **Table 5.2**.

Double melting peaks appear in DSC curves of PLLA-CR0.5+HR1, PLLA-CR0.5+HR5 as shown in **Figure 5.4**. When heating rate is 10°C/min, T_{mI} becomes so dominant that T_{mII} is observed only as a shoulder. T_{mI} increases with heating rates, while T_{mII} decreases, but only very slightly. However, the ratio of ΔH_{mI} and ΔH_{mII} increases significantly with increasing heating rates, which is consistent with the mechanism of melt-recrystallization. It is suggested by the melt-recrystallization

Table 5.2 The Occurrence of Double Melting Peaks in the Subsequent Heating Scans of Non-isothermally Melt-crystallized PLLAs at Different Cooling Rates

	CR0.5	CR1	CR2	CR3	CR4	CR5	CR10	CR20
HR1	✓	X	X	X	X	X	X	X
HR5	✓	X	X	X	X	X	X	X
HR10	✓	✓	X	X	X	X	X	-
HR20	-	✓	X	X	X	X	-	-
HR30	-	-	X	X	X	X	-	-

✓: $T_{mI}+T_{mII}$

X: $T_{cII}+T_{mII}$

- : T_{mI} only

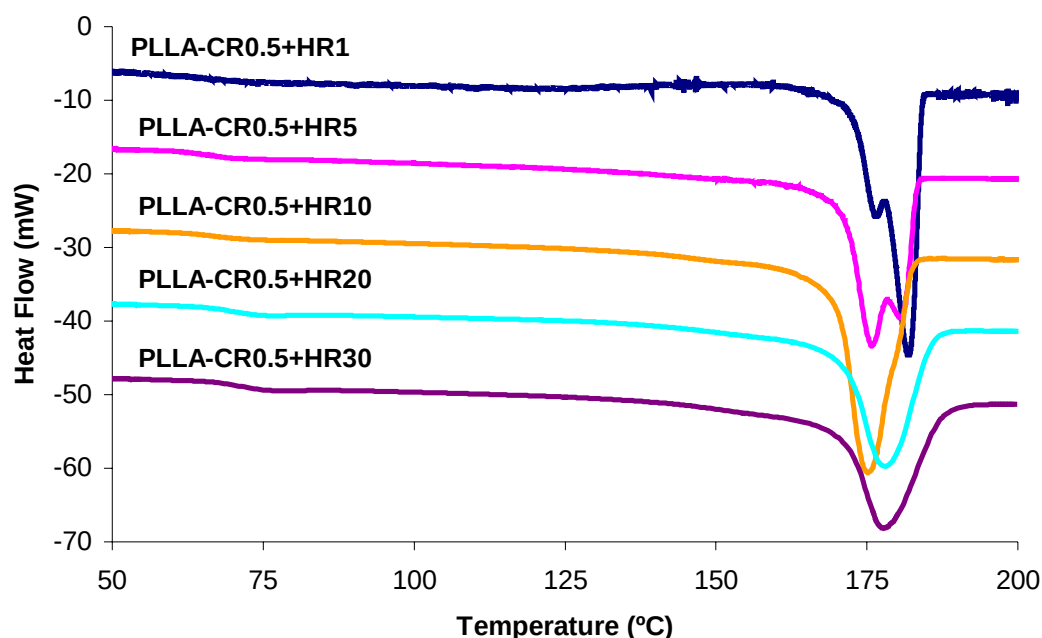


Figure 5.4 DSC Heating Scans at Different Heating Rates after Non-isothermal Melt-crystallized at 0.5°C/min

model that small and imperfect crystals change successively into more stable crystal through the melt-recrystallization mechanism. Because melting and recrystallization are competitive in the heating process, recrystallization is suppressed by higher heating rates. Thus, there are less recrystallized crystals formed (reduced ΔH_{mII}) with less quality (lowered T_{mII}), while more original crystals melt (increased T_{mI} and ΔH_{mI}). And eventually when the heating rate is high enough to completely inhibit the recrystallization, only one melting peak will be observed, as in the case of PLLA-CR0.5+HR20 and PLLA-CR0.5+HR30. The peak temperature is higher than the T_{mI} of PLLA-CR0.5+HR10 due to superheating.

Figure 5.5 shows an apparently different appearance of the DSC curves for samples heated at different rates after being cooled at 1°C/min from the melt. It seems

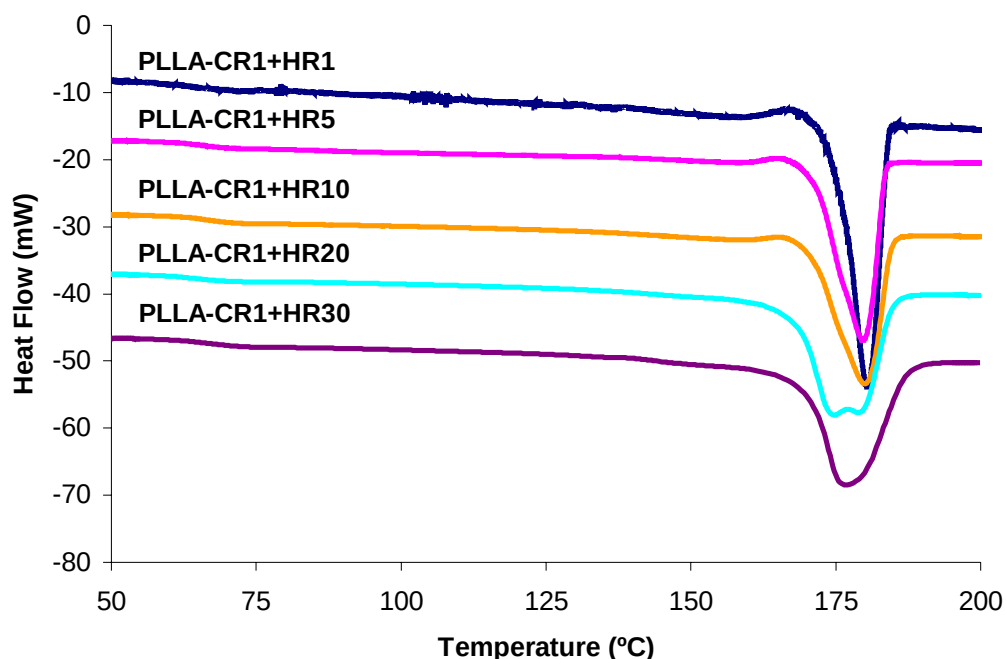


Figure 5.5 DSC Heating Scans at Different Heating Rates after Non-isothermal Melt-crystallized at 1°C/min

that when heated up at 1°C/min (PLLA-CR1+HR1), 5°C/min (PLLA-CR1+HR5), and 10°C/min (PLLA-CR1+HR10), an exothermic peak, T_{cII} was observed just before the melting, T_{mII} . Although only single melting peak is observed, the existence of small exothermic peak suggests the close competition of simultaneous melting and recrystallization processes and that T_{mI} is just too weak and broad to be observed. The changes in T_{mI} and T_{cII} are really gradual and insignificant unless viewed in different scales, as in **Figure 5.6(a)-(c)**. The melting slowly overpowers recrystallization as heating rate increases. At heating rate of 20°C/min, double melting of almost equal size peaks appears, while T_{cII} disappears. At even higher heating rate of 30°C/min, two peaks overlap so severely that only T_{mI} is observed.

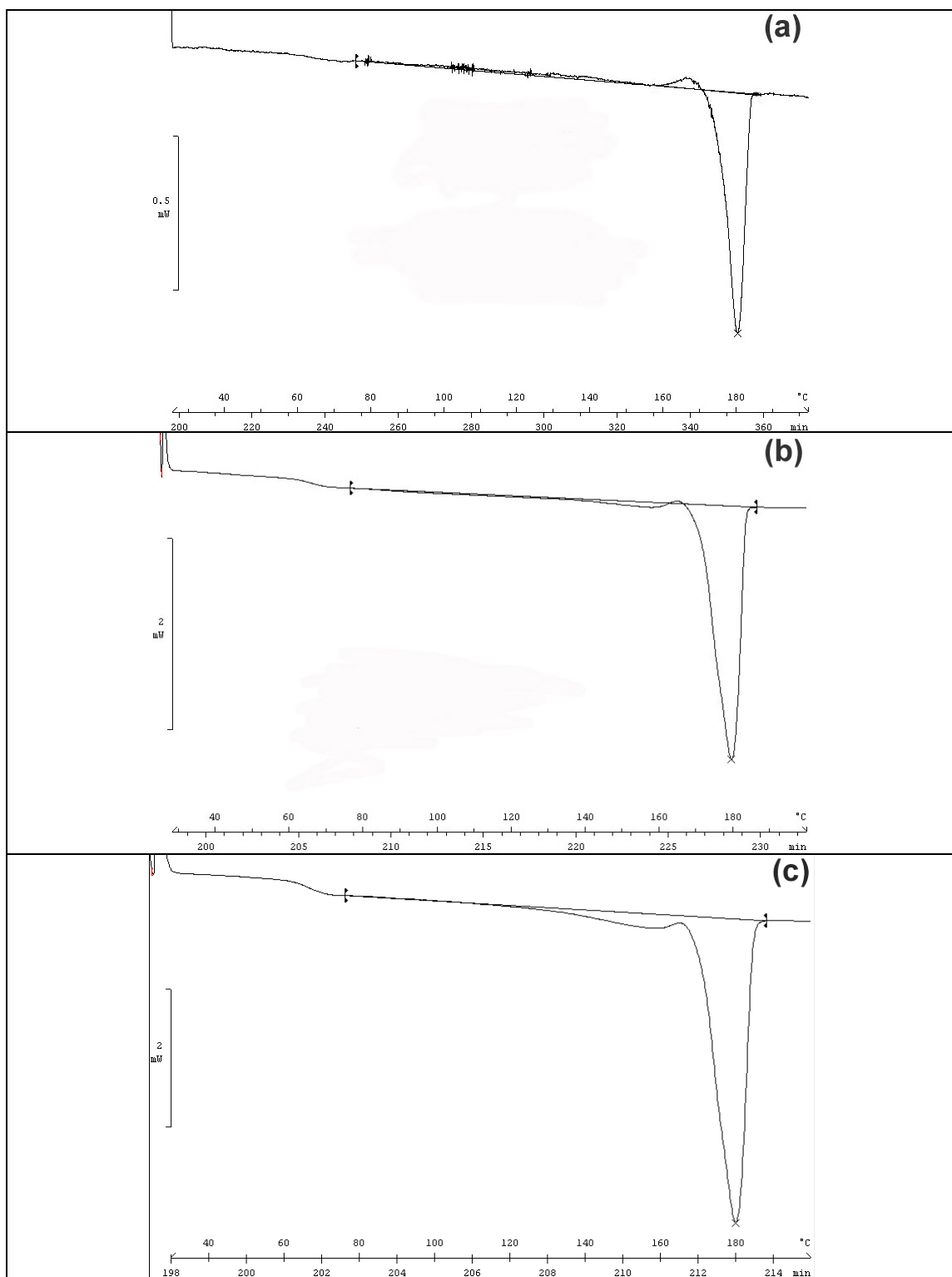


Figure 5.6 Individual DSC Thermographs of (a) PLLA-CR1+HR1, (b) PLLA-CR1+HR5, and (c) PLLA-CR1+HR10 with Baselines

For samples non-isothermally melt-crystallized at cooling rate 2°C/min, 3°C/min, 4°C/min and 5°C/min, similar trends are observed within slightly different extent. All DSC curves of these samples show no obvious double melting peak is observed at any heating rate, but a T_{cII} prior to the T_{mII} , as in the representative **Figure 5.7**. The size of T_{cII} decreases with the heating rate, sharing the same characteristic as demonstrated in **Figure 5.6(a)-(c)**, which implies the weakening of melt-recrystallization mechanism. Meanwhile, T_{cII} increases slightly from 160°C to 165°C with increasing heating rates, while T_{mII} decreases, but just barely; it is almost constant around 179°C within experimental errors.

Except for those samples cooled from melt at less than 2°C/min, a cold crystallization peak, T_{cI} , and glass transition temperature, T_g , start to show in the subsequent heating scans for those samples obtained at higher cooling rates, as seen in **Figure 5.7**. T_{cI} moves to higher temperature and becomes broader with increasing heating rate. For PLLA-CR3+HR30, T_{cI} is only observable in enlarged view in **Figure 5.8**, although the temperature is difficult to determine. As the cooling rate continues to rise, the size of resultant T_{cI} increases accordingly when more crystals resume crystallization during the heating process.

When non-isothermal cooling rate further increases to 10°C/min and 20°C/min, the crystallinity is close to zero. The resultant curves of heating rate effect (**Figure 5.9**) are virtually the same as those obtained for original amorphous films, shown in **Figure 2.4**. The double cold-crystallization, T_{cI} and T_{cI}' , occurs as well, which was believed to be the net effect of cold-crystallization and the onset of melt-

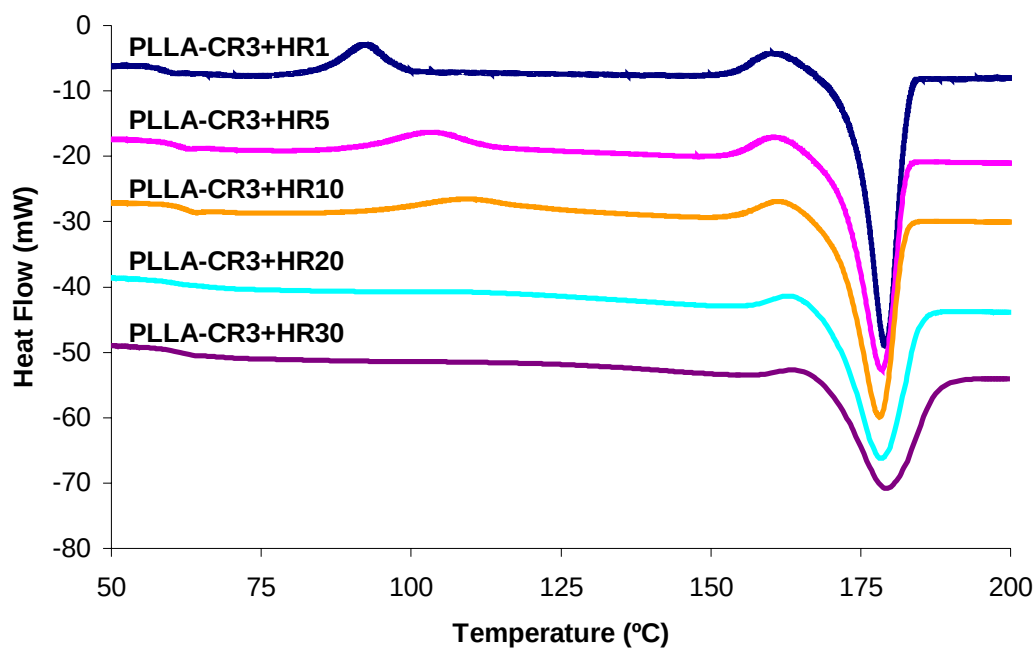


Figure 5.7 DSC Heating Scans at Difference Heating Rates after Non-isothermal Melt-crystallization at 3°C/min

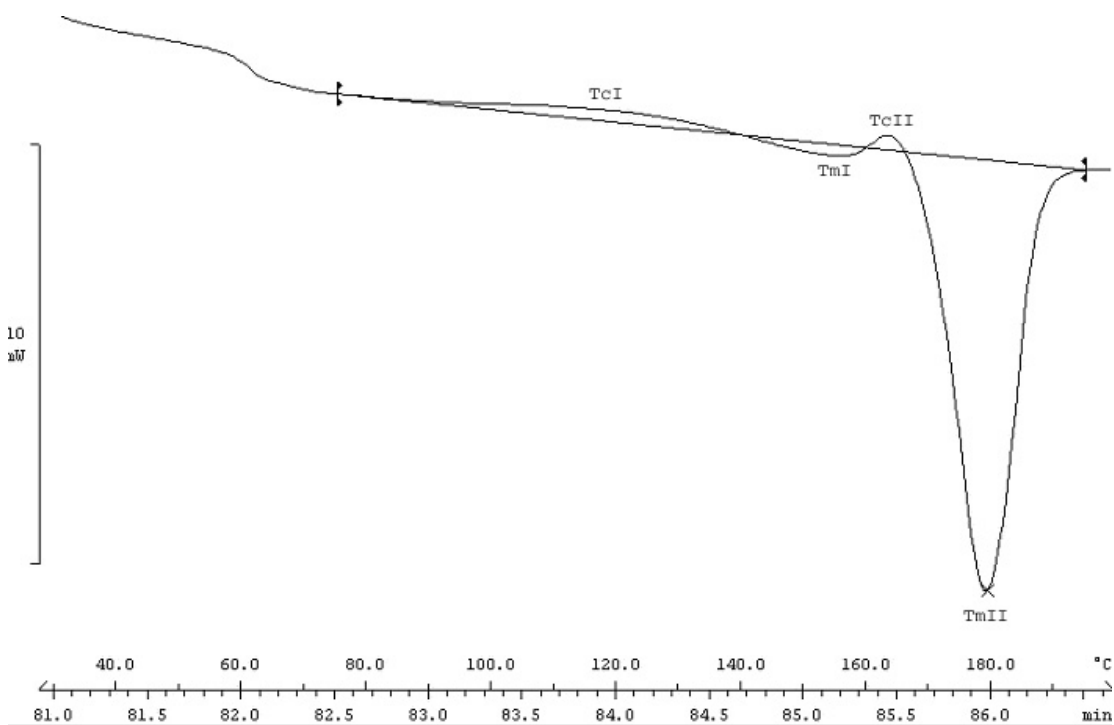


Figure 5.8 DSC Thermograph of PLLA-CR3+HR30

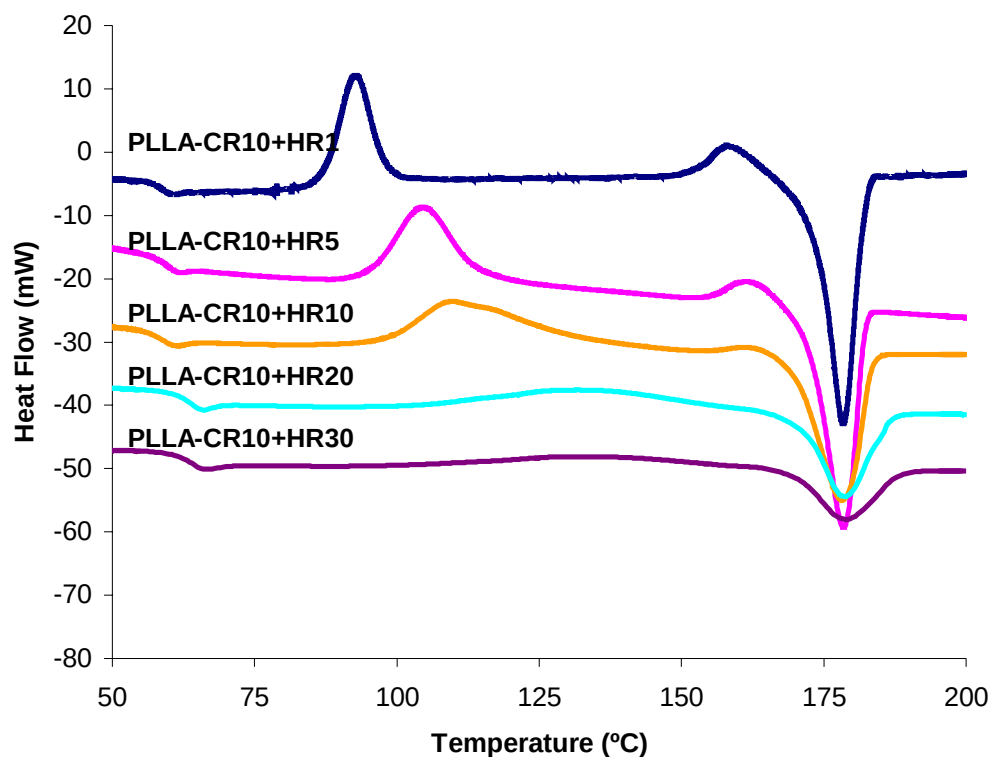


Figure 5.9 Second DSC Heating Scan at Difference Heating Rate after Cooling Down from the Melt at 10°C/min

recrystallization. When heating rate is over 20°C/min, double melting behavior is no longer detected.

Overall, our results seem similar to the findings of Yasuniwa et al.¹²², who used a PLLA with molecular weight 3×10^5 and in the form of pellets. They claimed that the appearance of the double melting peaks depends largely on matching cooling rate and heating rate, which is beyond the usual experimental conditions, and is the reason why it was not reported earlier. Their CR-HR map shows two areas that double melting is observed, one being “low CR + low HR” combination, which is recognized from heating rate lower than 3°C/min, and the other being “high CR + high

HR”. They relate the first combination to melt-recrystallization, while they did not study the second group due to the broadness and overlapping of the peaks, and the low quality DSC curves. However, they have considered the cases where a T_{cII} occurs prior to T_{mII} , $T_{cII}+T_{mII}$, as single melting, not as a non-typical double melting behavior, where T_{cII} overwhelms T_{mI} and can only be separated in TMDSC. As a result, in our study, under many CR+HR combinations, although we may not observe the distinctive double melting phenomena, PLLA still undergoes continuous melt-recrystallization procedure, and shows $T_{cII}+T_{mII}$ instead. It seems, in general, the same sample would go through $T_{cII}+T_{mII}$ at a lower heating rate, then at a higher rate, $T_{mI}+T_{mII}$. Eventually, at an even higher heating rate, the disappearance of double melting.

Also from our observation, it is observed that even though crystallization can be completed at about 40% crystallinity (PLLA-CR2) without obvious cold crystallization peak showing in the subsequent heating scan; the crystals are still not perfect enough to avoid melt-recrystallization to take place. Even when the initial crystallinity reaches as high as 63% (PLLA-CR0.5), the samples still went through reorganization when heated up below 10°C/min, trying to reach an even more perfect state. When cooling rate reaches 10°C/min and 20°C/min, if the heating rate is also high, then no double melting is observed, possibly covered under the very broad cold-crystallization process.

5.2 ISOTHERMAL CRYSTALLIZATION FROM THE MELT

5.2.1 Samples crystallized at different temperatures for 1 hr

The overall DSC thermograms of PLLAs isothermally melt-crystallized at different T_{mc} are demonstrated in **Figure 5.10** and the temperatures of the major effects are tabulated in **Table 5.3** (the crystallinity values listed are approximated by dividing ΔH_{cI} , ΔH_{cII} , and overall ΔH_m with Fischer's value of 93 J/g¹¹⁵ for ΔH_m^0). T_{mc} is also chosen from 80°C to 160°C with an increment of 10°C as its cold-crystallization counterpart in section 4.2.1. The appearance of **Figure 5.10** presents great similarity to **Figure 4.8**, which dealt with isothermal cold-crystallization samples, except for the curves of PLLA-MC140, 150 and 160 whose crystallization does not complete within 60 minutes in the case of melt-crystallization. This difference from its cold-crystallized counterpart is due to the fewer nuclei existing in the melt-crystallized samples, which results in slow crystallization kinetics at high temperatures. ΔH_{cI} of PLLA-MC80 is significantly smaller than that of PLLA-CC80 (13.2% vs. 33.9% crystallinity) for the same reason. The rest of the curves, i.e. PLLA-MC90, 100, 110, 120 and 130 exhibits close resemblance to their cold-crystallization counterpart, in terms of percentage crystallinity, peak temperatures, the discontinuity at 120°C, as well as the progress in the change of peak characteristics.

The crystallization of PLLA-MC80, 140, 150, 160 does not complete in 60 minutes, showing a clear glass transition peak, T_g , a broad exothermic “cold-crystallization” peak, T_{cI} , and a second exothermic crystallization peak, T_{cII} , just prior to the final melting. It is interesting to note that although ΔH_{cI} of PLLA-MC80 is

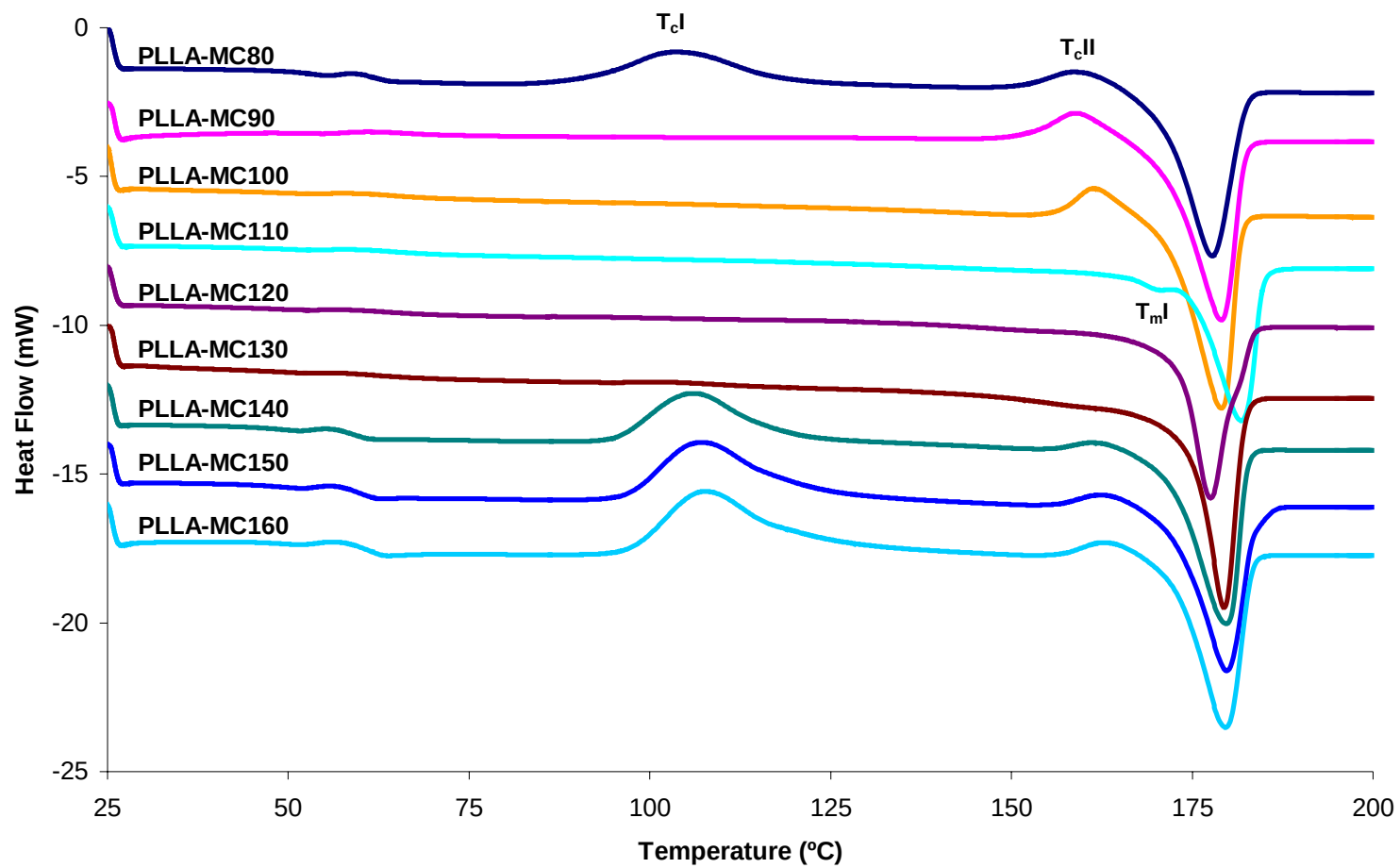


Figure 5.10 DSC Thermograms of PLLA Melt-crystallized at Different Temperatures for 60 minutes, 10°C/min

Table 5.3 Summary of Observed Thermal Effects of PLLA Melt-crystallized at Different Temperatures for 60 Minutes (°C) and the Degree of Crystallinity

	T_{cI}	$X_{c,TcI}$	T_{mI}	T_{cII}	$X_{c,TcII}$	T_{mII}	$X_{c,h}$
PLLA-MC80	103.47	25.8%	-	158.94	5.2%	177.91	13.2%
PLLA-MC90	-	-	-	158.82	5.0%	178.66	40.0%
PLLA-MC100	-	-	-	161.44	5.1%	179.20	48.2%
PLLA-MC110	-	-	169.87	-	-	181.50	53.8%
PLLA-MC120	-	-	177.14	-	-	-	54.9%
PLLA-MC130	-	-	179.06	-	-	-	59.3%
PLLA-MC140	105.99	31.5%	-	161.41	1.2%	179.46	17.6%
PLLA-MC150	107.17	42.0%	-	162.42	2.5%	179.48	4.7%
PLLA-MC160	107.68	45.1%	-	162.78	3.2%	179.32	1.2%

smaller than that of others, its ΔH_{cII} is actually larger, as listed in **Table 5.3** as well. This confirms our previous finding that temperature plays an important role in the crystallization of PLLA, even when less crystallization took place at higher treatment temperatures, the resultant crystals are still more perfect due to high chain mobility and less recrystallization in the subsequent heating scans.

The DSC scans of PLLA-MC90 and 100 also reveal crystallization peak T_{cII} although the absence of T_{cI} suggests the completion of crystallization before the heating scan. This observation further supports what we found before in the samples obtained through non-isothermal melt-crystallization at slow cooling rates like -0.5°C/min, -1°C/min, and -2°C/min. That is, no matter whether the crystallization is completed or not under the treatment conditions, as long as the crystals formed retain certain extent of imperfection, T_{cII} or double-melting will by all means show up during the subsequent heating scan as a result of the emergence of the continuous melt-recrystallization process.

The curve of PLLA-MC110 shows close similarity to that of PLLA-CC110, i.e. double melting is clearly observed, with T_{mI} and T_{mII} at 169.87°C and 181.50°C, respectively. Also ΔH_{mII} is significantly larger than ΔH_{mI} . At $T_{mc}=110^\circ\text{C}$, due to the enhancement of crystal perfection at this temperature, less amount of reorganization is needed. The peak temperatures are a bit higher than its cold-crystallized counterpart because more perfect crystals usually form from the melt than from the glassy state at the same temperature and duration. T_{mII} of samples melt-crystallized from 80°C to 110°C increases, as more perfect crystals are generated during the heating scan.

When treated at $T_{mc}=120^\circ\text{C}$, the melt-recrystallization is largely limited at 10°/min heating rate due to the perfection of original crystals, so that only a broad shoulder was vaguely observed to the right of the main melting peak, T_{mI} . As treatment temperature reaches 130°C, only a sharp single melting temperature is detected where melt-recrystallization can be considered as finally suppressed.

It is noteworthy that the discontinuity Ohtani et al.¹²³ observed at 120°C, when only major melting points of treated samples are plotted as a function of the corresponding cold-crystallization temperature, is observed not only for our cold-crystallized but also melt-crystallized samples if plotted in the same manner as in **Figure 5.11**. Based on their wide-angle x-ray patterns, they believe β - and α -crystals formed below and above 120°C, respectively. They have attributed T_{cI} to cold-crystallization of β -form, and T_{cII} to the phase transition to a more stable crystal form.

No matter how complicated the thermal events involved, our WAXD patterns of each crystallized sample still indicate that they can be explained on the basis that

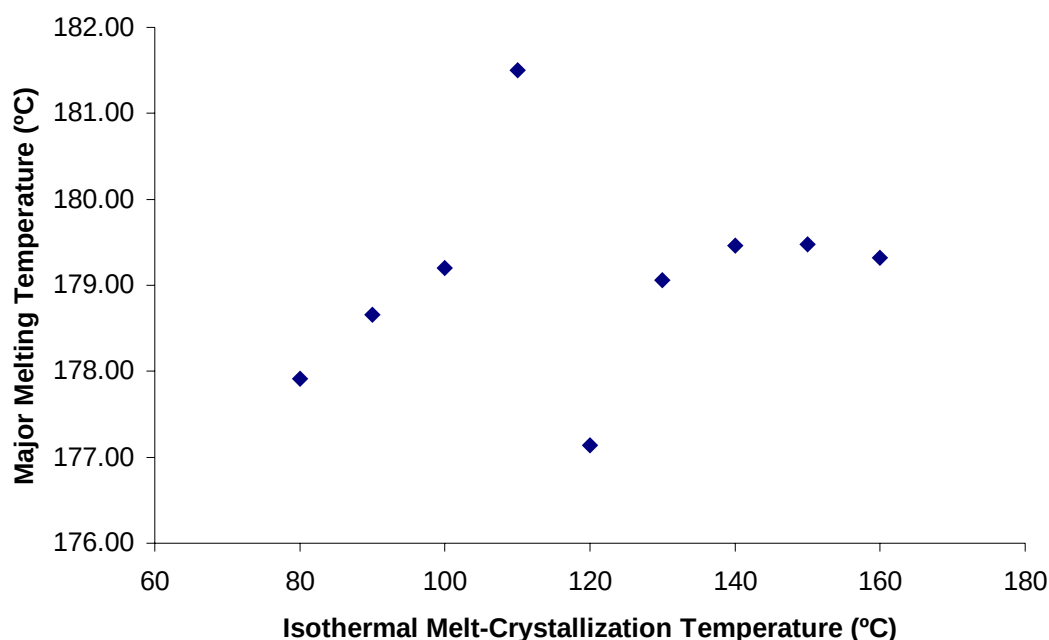


Figure 5.11 Major Melting Temperatures as a Function of Isothermal Melt-crystallization Temperatures of PLLAs

mainly the α -crystal form exists, though the crystals are more imperfect at higher and lower temperatures compared to that formed in the neighborhood of 130°C, as illustrated in **Figure 5.12**. PLLA-MC150 and 160 are almost amorphous from the WAXD patterns, which is consistent with their low crystallinity values estimated from DSC. Combined with **Figure 5.10**, it seems that when (103), (011), (211) peaks are not at all distinguished, in the case of $T_{mc} < 110^\circ\text{C}$ or $T_{mc} > 140^\circ\text{C}$, the imperfect crystals formed would experience melt-recrystallization, showing distinctive recrystallization peak, T_{cII} , prior to final melting, T_{mII} , in DSC scans. The melting and recrystallization of imperfect crystals start almost simultaneously, and recrystallization overwhelms melting so that T_{mI} does not show up at all. These observations are all in agreement with its cold-crystallization counterpart. The peak at $2\theta = 24.5^\circ$ still seems

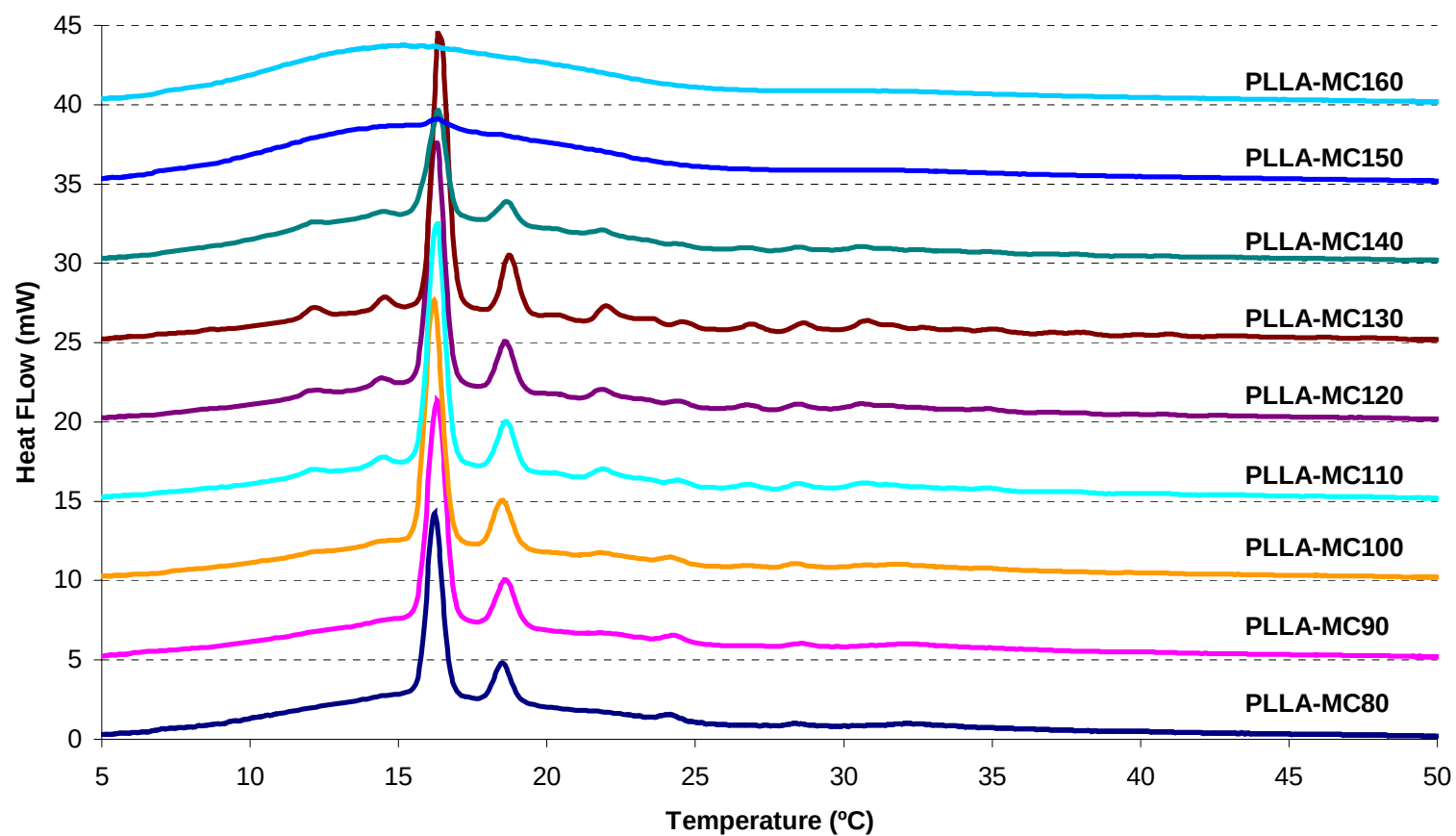


Figure 5.12 WAXD Patterns of PLLA Melt-crystallized at Different Temperature for 60 minutes

to persistently appear as in the cold-crystallization samples, and its intensity does not change as melt-crystallization temperature increases except when the crystallinity is close to zero. This suggests the possibility of the presence of δ -phase in some of the melt-crystallized samples as well.

However, when we examine the patterns of PLLA-MC140 and 80 closely, with similar crystallinity values reflected in DSC, PLLA-MC140 actually shows a bit trace of (103), (011), (211) peaks, while PLLA-MC80 shows none. This indicates the perfection of crystals is better when formed at higher temperature, which is consistent with the corresponding SAXS results, as shown in **Figure 5.13** and **Table 5.4**. While the periodicity is clearly revealed for PLLA-MC140, no long period exists for PLLA-MC80. This latter feature is similar to that observed for the PLLA-CC80 sample.

5.2.2 Samples crystallized at 140°C for different period of time

DSC thermograms of samples isothermally melt-crystallized at 140°C for different period of time are presented in **Figure 5.14**. The crystallization does not complete if $t_{mc} < 120\text{min}$, as indicated in the broad “cold-crystallization” peak, T_{cI} , in **Figure 5.14**. And the longer the t_{mc} is, the smaller ΔH_{cI} is, as expected. ΔH_{cII} decreases as well, although very insignificantly. However, T_{cII} is only observed in samples treated for 60 minutes or less and sample treated for 75 minutes shows only a vague double-melting peak below the baseline, which is not so clear due to the scale of the figure. A separate **Figure 5.15** shows the detail. Meanwhile, T_{mII} increases gradually from 178°C to 183°C with increasing t_{mc} as seen in **Table 5.5**. The WAXD

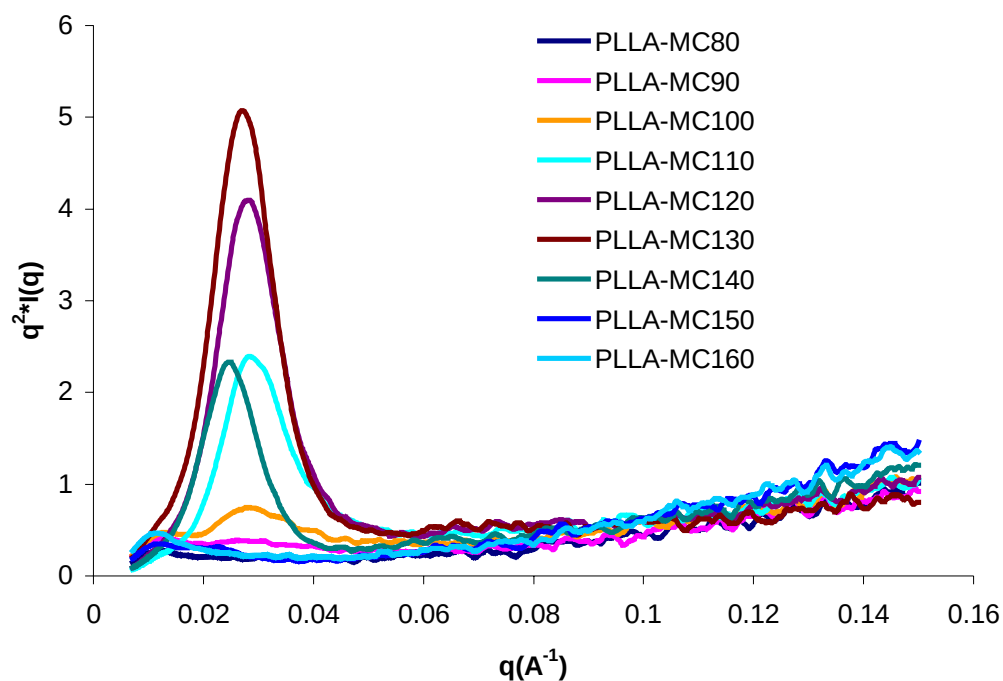


Figure 5.13 Lorentz corrected SAXS of PLLA Melt-crystallized at Different Temperature for 60 minutes

Table 5.4 Long Period and Lamellar Thickness of PLLA Melt-crystallized at Different Temperatures for 60 minutes

	$q_{\max} (\text{\AA}^{-1})$	$L_{\max} (\text{\AA})$	$l_c (\text{\AA})$
PLLA-MC80	-	-	-
PLLA-MC90	-	-	-
PLLA-MC100	0.028304	221.99	107.00
PLLA-MC110	0.02831	221.94	119.29
PLLA-MC120	0.028309	221.95	121.85
PLLA-MC130	0.027083	232.00	137.58
PLLA-MC140	0.024662	254.77	44.84
PLLA-MC150	-	-	-
PLLA-MC160	-	-	-

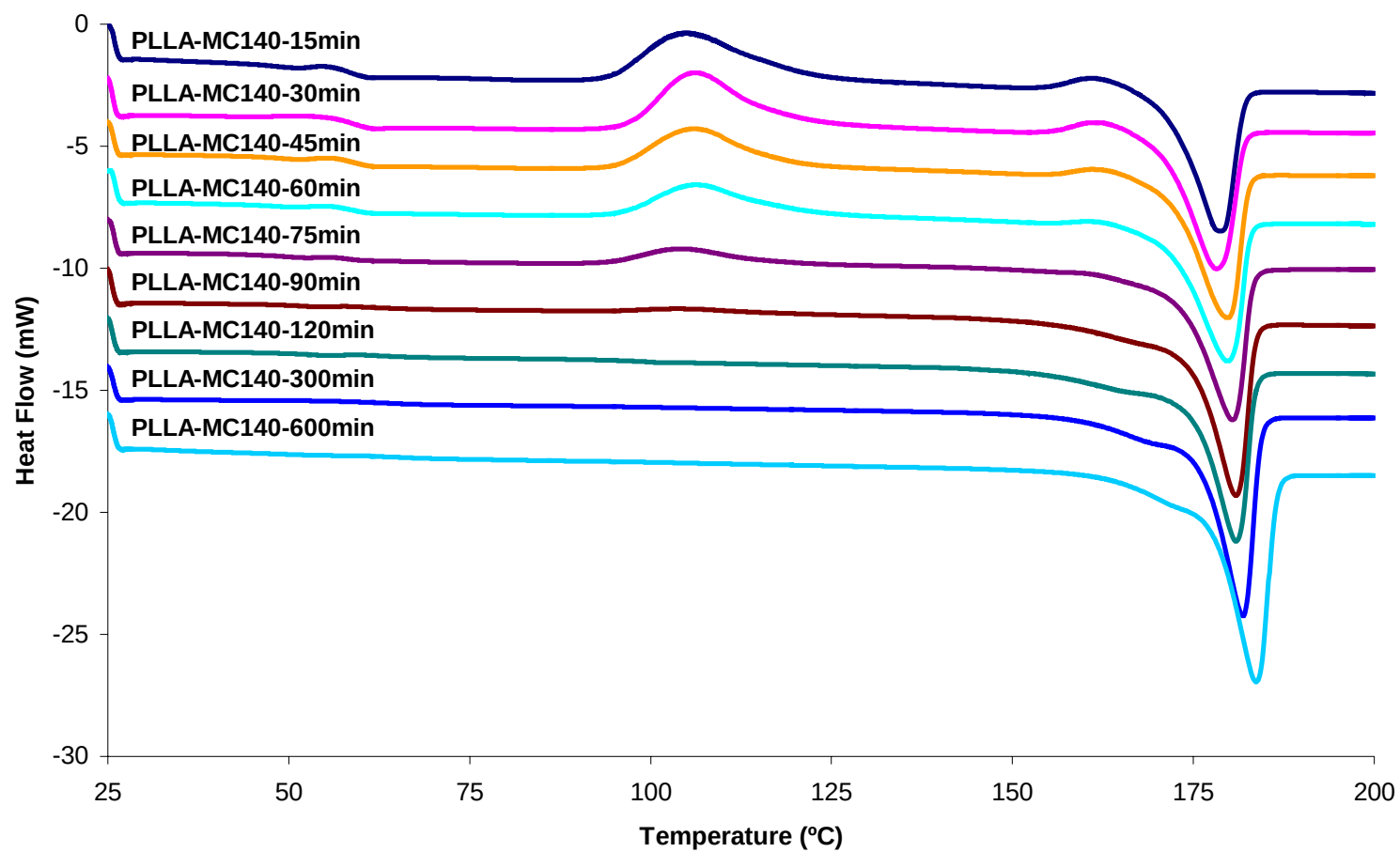


Figure 5.14 DSC Thermograms of PLLA Melt-crystallized at 140°C for Different Period of Time, 10°C/min

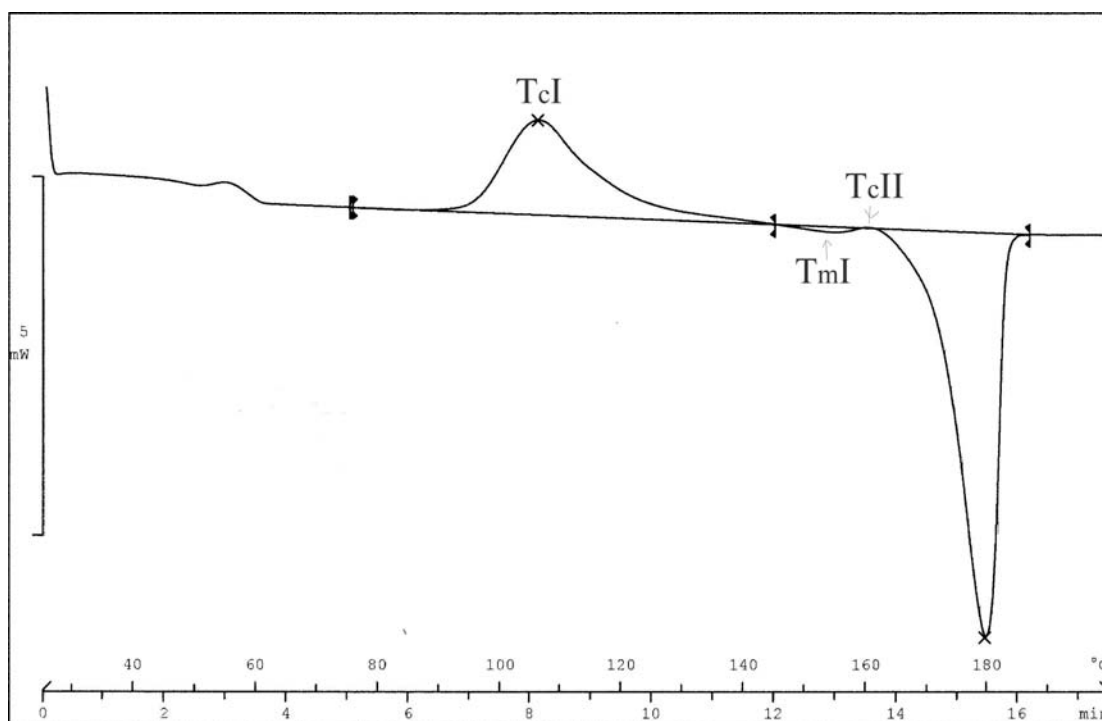


Figure 5.15 DSC Thermogram of PLLA-MC140-75min

Table 5.5 Summary of Observed Thermal Effects of PLLA Melt-crystallized at 140°C for Different Period of Time (°C) and the Degree of Crystallinity

	T_{cI}	T_{mI}	T_{cII}	T_{mII}	X_{ch} (%)
PLLA-MC140-15min	104.82	-	160.90	178.28	0.0%
PLLA-MC140-30min	105.17	-	161.09	177.97	2.8%
PLLA-MC140-45min	105.34	-	160.92	178.31	7.7%
PLLA-MC140-60min	105.99	trace	161.41	179.46	17.6%
PLLA-MC140-75min	105.31	trace	-	179.31	24.9%
PLLA-MC140-90min	trace	-	-	180.12	47.3%
PLLA-MC140-120min	trace	-	-	180.41	57.7%
PLLA-MC140-150min	-	-	-	180.57	65.9%
PLLA-MC140-300min	-	-	-	181.36	69.2%
PLLA-MC140-600min	-	-	-	183.16	75.4%

patterns of these samples, **Figure 5.16**, show almost no crystalline peaks when treated less than 45 minutes. The crystals start to develop when treated over 60 minutes, it seems the longer the t_{mc} , the more perfect the crystals get judging from the development of peaks like (103) (011) and (113)/(203). SAXS data from these samples, **Figure 5.17** and **Table 5.6**, are also in agreement with the development of crystal perfection over time. One important observation is that, at $t_{mc}=90$ and 120min, even though crystallization is not completed, the crystals are perfect enough to give sharp WAXD peaks and most of all, showing no T_cII . That is, although the crystallization is not completed within time allowed, the crystals are perfect enough not to undergo reorganization process during heating.

From the SAXS data, **Table 5.6**, it is clear that once a long period is established at certain crystallization temperature, it does not change appreciably with treatment time, t_{mc} . Crystal thickness, on the other hand, increases rapidly with t_{mc} , while at the expense of amorphous layer thickness. This, of course, is consistent with the rapid increase in crystallinity shown in **Table 5.5**.

5.3 SUMMARY

When PLLA is non-isothermally crystallized from the melt at different cooling rate, only a single crystallization peak is observed, which ensured the unimodal size distribution of crystals in the resultant samples. The study of heating rate effect on these samples suggests that double melting, although often hidden as non-typical T_cII+T_mII , occurs under many experimental conditions, even when initial crystallinity of the sample is already fairly high.

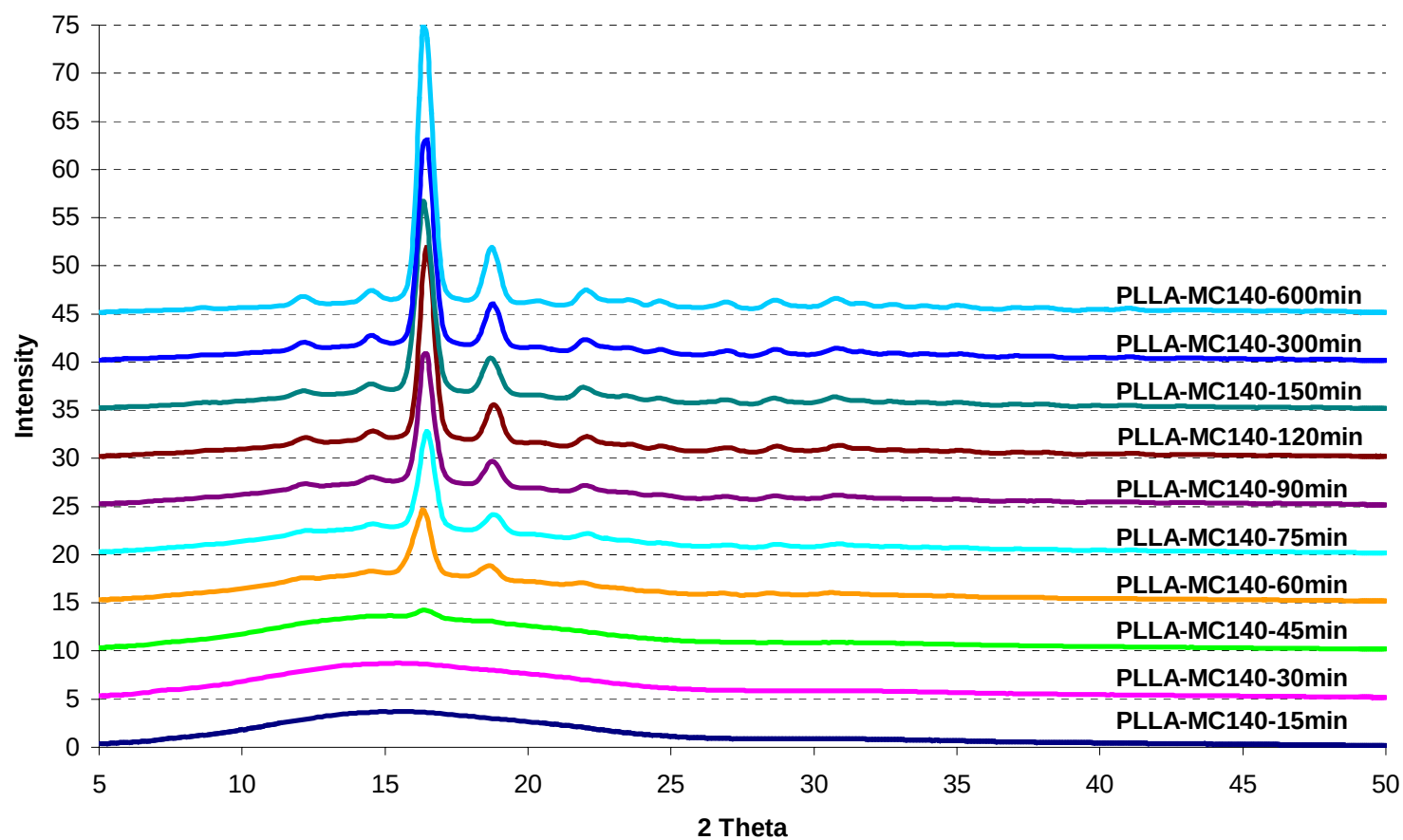


Figure 5.16 WAXD Patterns of PLLA Melt-crystallized at 140°C for Different Period of Time

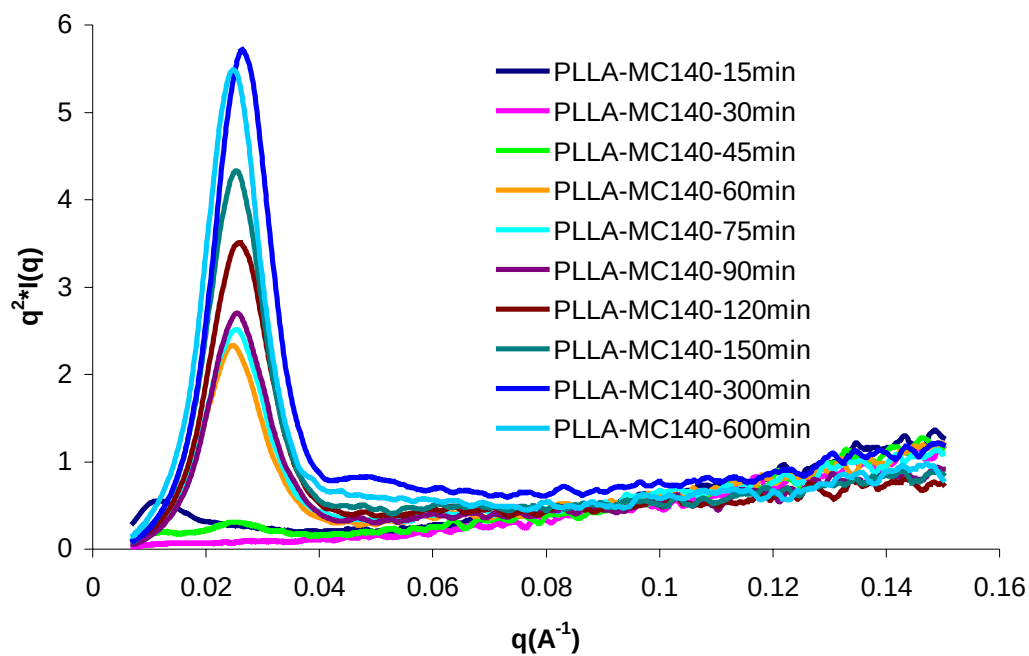


Figure 5.17 Lorentz Corrected SAXS of PLLA Melt-crystallized at 140°C for Different Period of Time

Table 5.6 Lorentz Corrected Long Period and Lamellar Thickness of PLLA Melt-crystallized at 140°C for Different Period of Time

	$q_{\max} (\text{\AA}^{-1})$	$L_{\max} (\text{\AA})$	$l_c (\text{\AA})$
mPLLA-MC140-15min	-	-	-
mPLLA-MC140-30min	-	-	-
mPLLA-MC140-45min	0.025005	251.28	19.35
mPLLA-MC140-60min	0.024662	254.77	44.76
mPLLA-MC140-75min	0.025347	247.89	61.65
mPLLA-MC140-90min	0.02552	245.21	115.43
mPLLA-MC140-120min	0.025867	242.90	140.13
mPLLA-MC140-150min	0.025357	247.79	165.87
mPLLA-MC140-300min	0.025512	245.28	170.33
mPLLA-MC140-600min	0.024826	253.09	190.85

At low crystallinity as 12% for PLLA-CR5, SAXS presents lamellar periodicity, while in contrast, PLLA-CC80-time samples that have crystallinity up to 40% do not possess it. This is due to the small size crystals formed at lower temperatures that is so scattered that lamellar structure cannot be established.

From the results collected so far, it becomes clear that the occurrence of double melting (including the cases that only $T_{cII}+T_{mII}$ is shown) only depends on the perfection of the crystals formed during the crystallization stage. It is not affected by whether the crystallization is completed or not within designated time indicated by the appearance of cold-crystallization peak T_{cI} . In some cases, T_{cII} appears even when the crystallization is completed (e.g. PLLA-MC90, PLLA-MC100). Or in other instances, T_{cII} disappears even when the crystallization is not completed (PLLA-MC140-90min, PLLA-MC140-120min). It is also not affected by the initial crystallinity, e.g. PLLA-CR0.5 sample reaches 63% crystallinity but still undergo melt-recrystallization process and shows double melting. In general, crystals of higher perfection will form when crystallized under higher temperature and prolonged period of time. As a result, melt-recrystallization will be avoided during the subsequent DSC scans.

CHAPTER 6 ESTIMATION OF EQUILIBRIUM MELTING TEMPERATURE AND HEAT OF FUSION OF PERFECT CRYSTAL

6.1 GIBBS-THOMSON METHOD FOR EQUILIBRIUM MELTING TEMPERATURE, T_m^0

According to Gibbs-Thomson equation, the intercept of the plot of melting temperature versus the reciprocal of the crystal thickness, l_c , determines the equilibrium melting temperature, T_m^0 , directly, when the fitted line is extrapolated to infinite lamellae thickness. **Figure 6.1** shows data for PLLA samples that were either melt- or cold-crystallized at different temperatures plotted in this fashion (related data of PLLA-CC110 ~ PLLA-CC160 and PLLA-MC110 ~ PLLA-MC130 are listed in previous chapters). T_m I is picked as the apparent melting temperature for the calculation. The resultant T_m^0 is approximately 207°C. Although the value is consistent with the literature values, even the same as Pyda's value¹³¹ that was derived from the same method with only 4 data points, the data scattering is noticeable. This leads to an uncertainty in the value of T_m^0 of about ± 3 degrees.

6.2 HOFFMAN-WEEKS METHOD FOR EQUILIBRIUM MELTING TEMPERATURE, T_m^0

Hoffman-weeks equation is usually the most convenient approach to estimate the equilibrium melting temperature, T_m^0 , from a series of melt-crystallized samples. Recrystallization is known to raise the apparent melting temperature, ultimately leading to the underestimation of T_m^0 . Consequently, difficulty arose due to the melt-recrystallization that existed in most of our melt-crystallized PLLA samples, so that we carefully chose the samples melt-crystallized at 115°C, 120°C, 125°C and

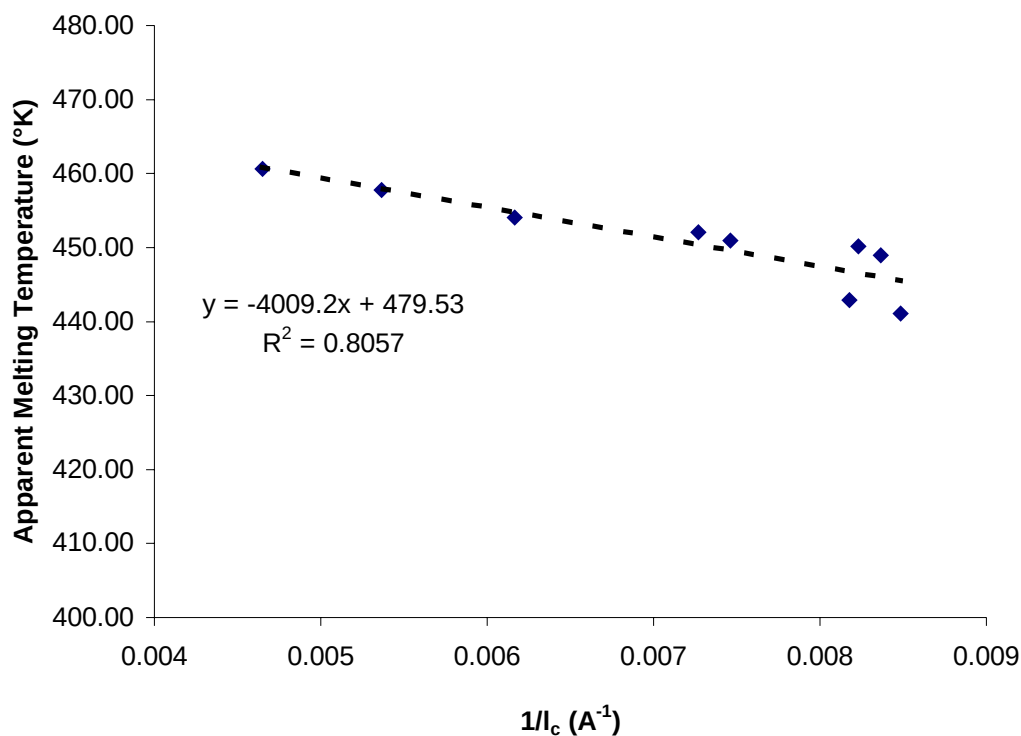


Figure 6.1 Apparent Melting Temperature vs. Inverse Lamellar Thickness of PLLA Melt- and Cold-crystallized at Different Temperatures

130°C, under which temperatures the recrystallization effect is believed to be minimal. According to **Figure 6.2**, the estimated $T_m^0 \cong 201^\circ\text{C}$, which is fairly close to the value proposed by Vasanthakumari and Pennings³³ shown in **Figure 2.25** and our value derived from the Gibbs-Thomson method. The β value is 1.66, which is in agreement with the theoretical expectation¹³⁵. However, the fact that β value is greater than unity indicates that possible secondary effects such as recrystallization and chain mobility still persist, but to a limited extent. As a result, T_m^0 can be slightly higher than 201°C.

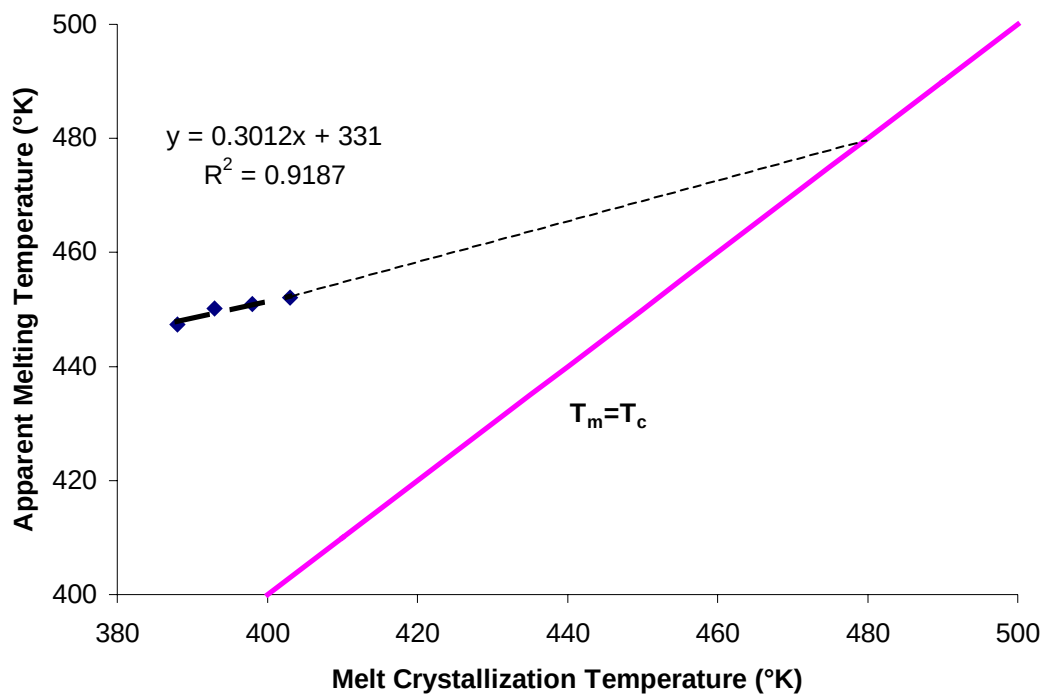


Figure 6.2 The Apparent Melting Temperature of PLLA as a Function of the Melt Crystallization Temperature from DSC, 10°C/min

Alternatively, we also used a series of cold-crystallized samples ($T_{cc} = 110^{\circ}\text{C} - 160^{\circ}\text{C}$) to plot the Hoffman-Weeks relationship and estimate T_m^0 , although this approach is rather unconventional. As demonstrated in **Figure 4.8**, T_mI occurs for all the isothermally cold-crystallized samples treated above 110°C . With 6 sufficient data points plotted in **Figure 6.3**, the estimated $T_m^0 = 204.5^{\circ}\text{C}$ and $\beta = 1.37$, which is also close to the literature value 207°C that was derived by Vasanthakumari and Pennings³³ from melt crystallized samples and from our own Gibbs-Thomson analysis. It seems that in the case of our amorphous PLLA films, both results from the cold-crystallized or melt-crystallized samples yielded estimation that is in reasonable agreement.

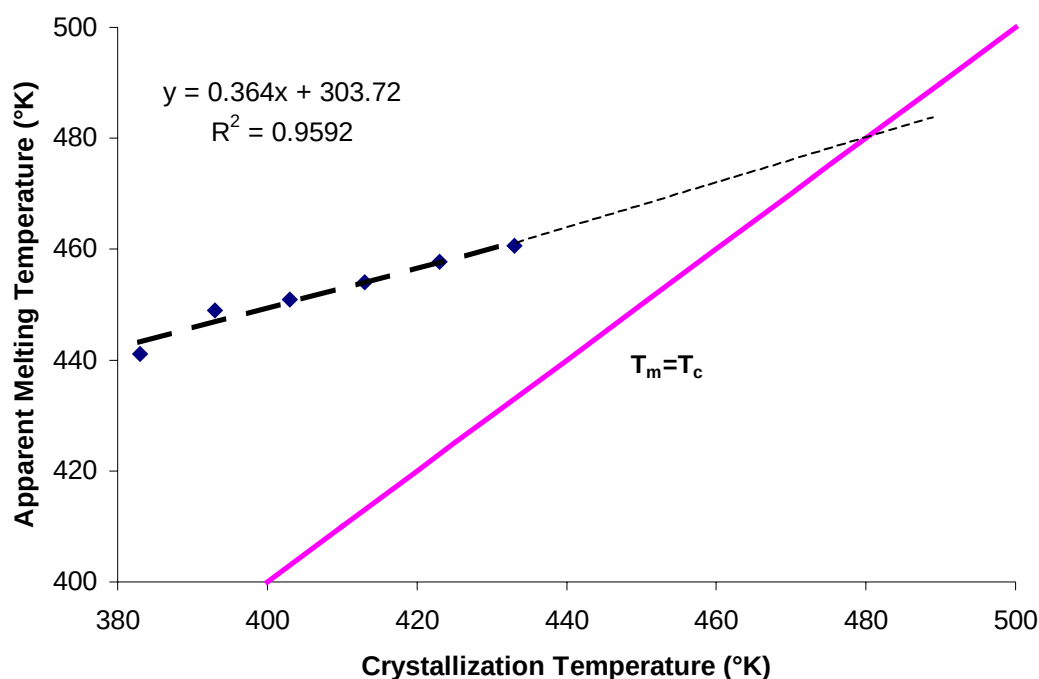


Figure 6.3 The Apparent Melting Temperature of PLLA as a Function of the Cold Crystallization Temperature from DSC, $10^{\circ}\text{C}/\text{min}$

6.3 FLORY METHOD FOR EQUILIBRIUM MELTING TEMPERATURE, T_m^0

We also attempted to determine T_m^0 based on variation of T_m with different molecular weights. As described in section 5.3, a series of PLLA samples with different molecular weights was prepared by holding the original PLLA sample at 210°C for different period of time before quenching into ice-water mixture. The molecular weights of these samples were determined by GPC. The reciprocal of apparent melting temperature was then plotted against the reciprocal of number average molecular weight according to Flory's equation, as shown in **Figure 6.4**. T_{mI} was selected for the construction of the plot, but T_{mII} is also plotted for reference purpose. T_m^0 derived from T_{mI} is 161.6°C for PLLA with infinite molecular weight,

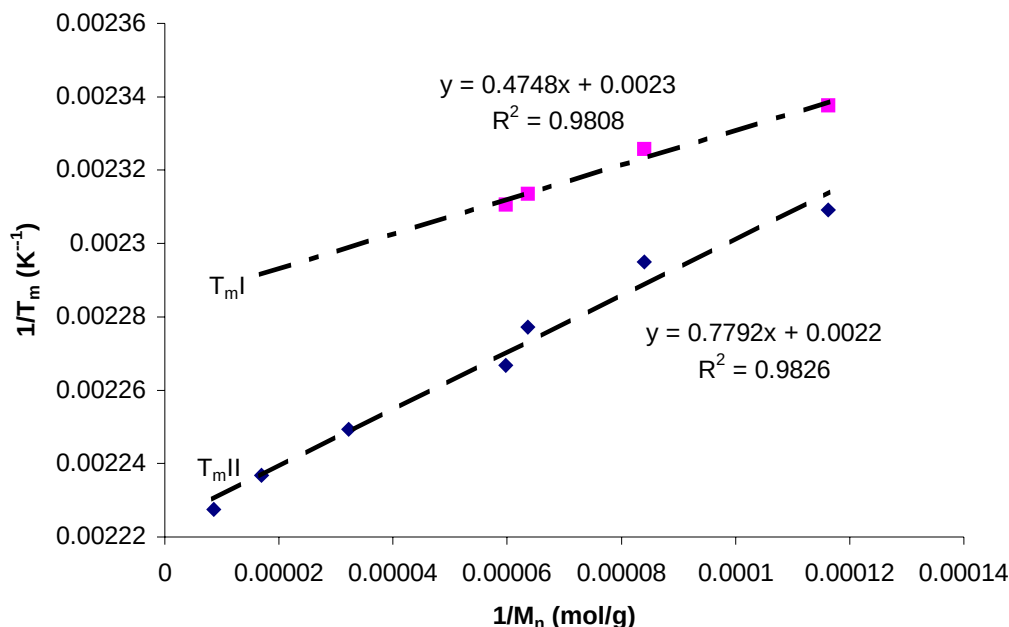


Figure 6.4 $1/T_m$ vs. $1/M_n$ for PLLA

which is similar to the value of Fischer et al.¹¹⁵ and is considerably lower than the value obtained from either the Gibbs-Thomson extrapolation or the Hoffman-Weeks method. Thus, there appears to be major inconsistencies between values obtained between the latter two methods and methods based on Flory's equation. Also notice that the value derived from T_{mII} is 181.4°C and close to Jamshidi et al.'s⁴⁰ result, but still significantly lower. At present we are uncertain what the cause of these inconsistencies is.

6.4 SPECIFIC VOLUME METHOD FOR EQUILIBRIUM HEAT OF FUSION, ΔH_M^0

One of the most conventional methods to obtain ΔH_M^0 is based on the linear relationship between heat of fusion measured in DSC and the specific volume of the same sample measured in DGC. The series of samples acquired from non-isothermal

melt crystallization had quite a spread in crystallinity values according to DSC results listed in **Table 5.1**. Heat of fusion from PLLA-CR series is thus plotted as a function of specific volume in **Figure 6.5**. As the crystalline density is 1.2762 g/cm^3 , based on the unit cell dimensions ⁷ from our previous research, the corresponding specific volume of 100% crystalline PLLA is $0.78358 \text{ cm}^3/\text{g}$. Extrapolating to this value, the heat of fusion turns out to be $90 \pm 4 \text{ J/g}$, which is consistent with the frequently quoted value of Fischer et al. ¹¹⁵ determined by a different method as discussed below.

6.5 FLORY METHOD FOR EQUILIBRIUM HEAT OF FUSION, ΔH_M^0

A second method to determine ΔH_m^0 is based Flory's theory, as detailed in section 2.4.1. Fischer et al. ¹¹⁵ obtained their value from a series of copolymers with

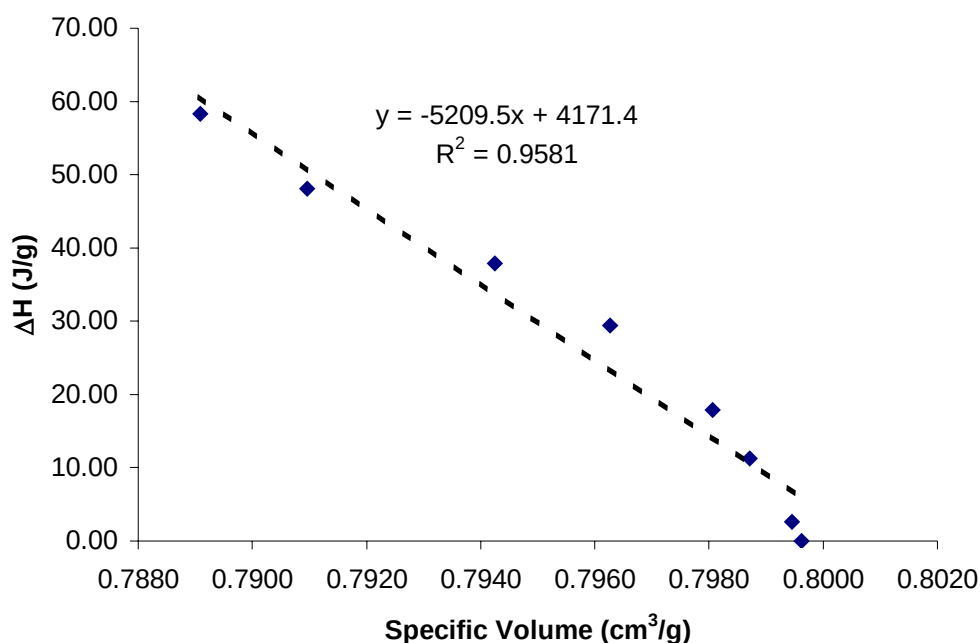


Figure 6.5 Heat of Fusion as a Function of Specific Volume for Samples that are Non-isothermally Cold-crystallized at Different Cooling Rates

different L-isomer content. Moreover, their value is calculated from T_{mI} instead of T_{mII} . Their original plot is hereby shown in **Figure 6.6**. An attempt to replot their data (**Table 6.1**) yields slightly different results. As we notice, their figure does not include all the 9 data points collected under supercooling 20°C condition, but only 6. **Figure 6.7** is a reproduction with all the 9 data, plus 5 data points collected under supercooling 9°C. **Figure 6.8**, on the other hand, uses the exact 6 points in that paper. The one point with the largest deviation from the straight line from the supercooling 9°C series is also omitted. The calculated equilibrium heat of fusion and melting temperature from each curve are tabulated in **Table 6.2**. It seems that under supercooling 20°C, the data have less deviation than 9°C, and the values yielded are consistent. However, T_m^0 estimated from this method is about 164°C, which seems to be significantly smaller than literature values, and the value obtained in the present research.

However, it is noteworthy that Fischer et al. 115 had admitted that although the ΔH_m^0 is in reasonable agreement with the value 81.2 J/g obtained from the DSC curves of the crystal by extrapolation to infinite crystal thickness, the application of Flory's equation to the above solution grown single crystals is rather meaningless. They claimed that Figure 6.6 simply demonstrates that this type of plotting is rather unspecific with regard to the supermolecular structure and that the melting behavior of solution grown crystals is similar to that of the bulk materials. Regardless of this comment, $\Delta H_m^0 = 93$ J/g is still the most popular value being used to calculate the

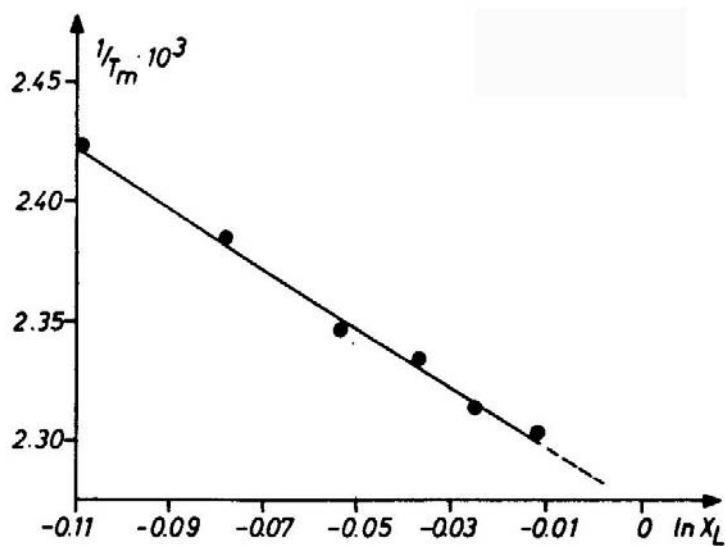


Figure 6.6 Plot of $1/T_m$ vs. $\ln X_L$ for the Single Crystals Obtained at 20°C Supercooling¹¹⁵

Table 6.1 Characteristic Data of the Lactide Copolymers, Data of Fischer et al.¹¹⁵

X_D (%)	X_L (%)	T_c (°C)	ΔT_u (°C)	T_m (°C)
0.6	99.4	88	20	165.6
1.15	98.85	83	20	160.9
2.4	97.6	78	21	159.1
2.75	97.25	75	21	156.2
3.65	96.35	73	20	155.2
5.2	94.8	69	20	153.0
5.7	94.25	65	20	149.3
7.5	92.5	57	20	146.1
10.3	89.7	49	20	139.5
0.6	99.4	99	9	166.4
2.75	98.85	65	9	163.3
5.2	94.8	80	9	157.5
7.5	92.5	68	9	153.2
10.3	89.7	60	9	138.8

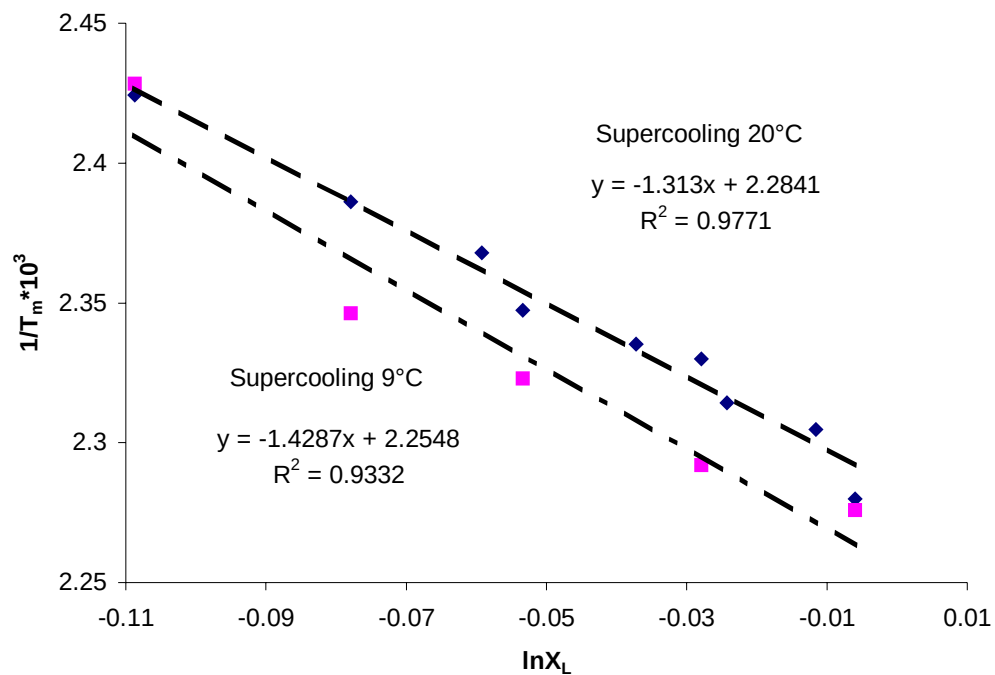


Figure 6.7 Plot of $1/T_m I$ vs. $\ln X_L$ for the Single Crystals Obtained at 20°C and 9°C Supercooling Using Fischer et al.'s Data ¹¹⁵

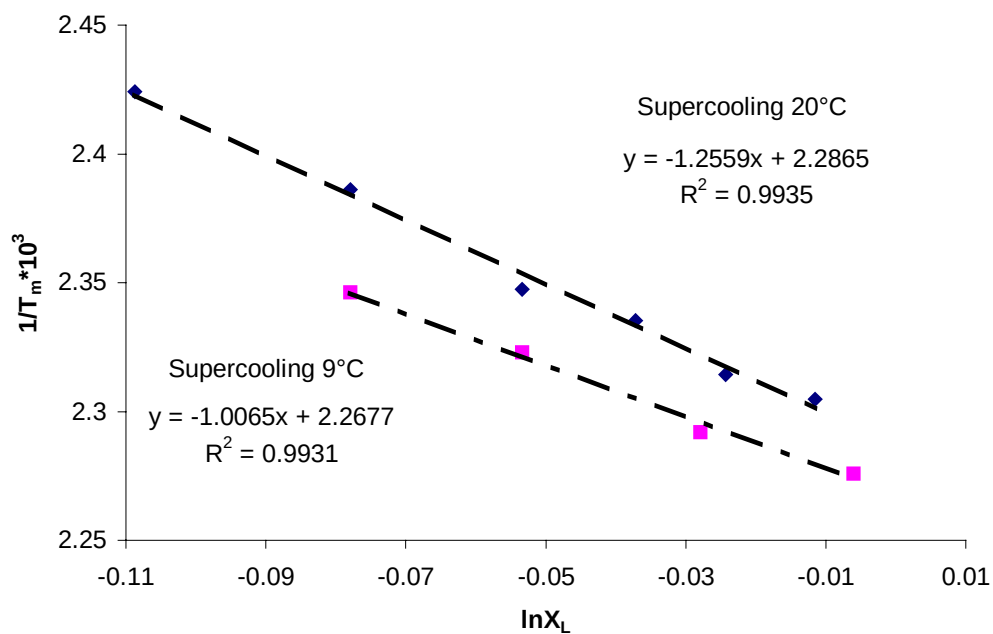


Figure 6.8 Modified Plot of $1/T_m I$ vs. $\ln X_L$ for the Single Crystals Obtained at 20°C and 9°C Supercooling Using Selected Fischer et al.'s Data ¹¹⁵

Table 6.2 Equilibrium Heat of Fusion and Melting Temperature Calculated from the Slopes and Intercepts of Curves in Figure 6.7 and 6.8

Supercooling	ΔH_m^0 (KJ/mol)	ΔH_m^0 (Kcal/mol)	ΔH_m^0 (J/g)	T_m^0 (°C)
20°C Fig6.7	6.33	1.51	87.9	164.8
9°C Fig 6.7	5.82	1.39	80.8	170.5
20°C Fig 6.8	6.62	1.58	91.9	164.3
9°C Fig 6.8	8.26	1.98	114.7	168.0

degree of crystallinity of PLAs, and is in fact close to what we determined from ΔH_m vs. specific volume extrapolation.

In section 6.3, we attempted to calculate the T_m^0 of PLLA with infinite molecular weight. ΔH_m^0 can also be estimated from each slope of **Figure 6.4** as 146.4 J/g and 89.2 J/g from T_{mI} and T_{mII} , respectively. This again shows the ambiguity to which the use of this approach can lead.

6.6 SUMMARY

Because of the good agreement between the value of T_m^0 determined from both the Gibbs-Thomson and the Hoffman-Weeks equations, we believe that the equilibrium temperature is fairly well established at $207 \pm 3^\circ\text{C}$.

The value of ΔH_m^0 obtained from ΔH_m as a function of specific volume is 90 ± 4 J/g, which is similar to the frequently quoted Fischer's value of 93 J/g.

The Flory method did not yield good estimations of either T_m^0 or ΔH_m^0 . It seems Gibbs-Thomson and Hoffman-Weeks methods are better for the estimation of T_m^0 for our PLLA. The specific volume method may also have an advantage over Flory method in cases that might otherwise be confused by double melting peaks,

provided 100% crystalline value is available with confidence. However, the exact reason for the evident deviation of results using Flory method remains uncertain at current time.

CHAPTER 7 SUMMARY AND CONCLUSIONS

The double melting behavior, which is often observed in semicrystalline polymers, of PLLA was investigated under various crystallization conditions: isothermal and non-isothermal crystallization from both the glassy state and the melt. Heating rate effect and partial melting were also studied to help elucidate the origin of double melting behavior. Meanwhile, the estimation of equilibrium melting temperature, T_m^0 , and equilibrium heat of fusion, ΔH_m^0 , was also performed.

Both the crystallization procedures and the subsequent melting were performed in a DSC cell with controlled temperature programs. WAXD and SAXS analysis were applied to the DSC crystallized samples to better understand the structural correlation with the double melting peaks. TMDSC was also used to separate the reversing and non-reversing thermal events, which are otherwise mixed in conventional DSC.

Upon non-isothermal cold-crystallization of original amorphous PLLA film at 10°C/min, a double cold-crystallization peak, labeled T_{cI} and T_{cI}' , appears at around 112°C and 119°C, respectively. Based on the analysis of DMA and TMDSC, the exhibition of this unconventional double cold-crystallization peak is believed to be associated with the net effect of conventional cold-crystallization and competing melt-recrystallization initiated a few degrees after the cold-crystallization. Another exotherm, T_{cII} , appears just prior to final melting when recrystallization overwhelms the melting of metastable crystals.

After various thermal treatments, up to two melting peaks were observed. Under many conditions, it is attributed to the melt-recrystallization process during the

heating in DSC. Without the help of TMDSC, the double melting endotherms, $T_{mI}+T_{mII}$, are not often observed, due to the overlap of T_{cII} and T_{mI} , which makes the observation and interpretation difficult. Instead, $T_{cII}+T_{mII}$ will appear. Such an observation is more prominent when the molecular weight is high.

Non-isothermal melt crystallization at different cooling rates exhibit only a single crystallization peak, excluding the existence of bimodal crystal size distribution in the resultant samples. Subsequent heating scans showed that the non-typical double melting occurs in many cases for PLLA melted under different heating rates, even when initial crystallinity of the sample is already fairly high.

The study of heating rate effect supports the assumption of melt-recrystallization during DSC scans. When the recrystallization process is suppressed by the increasing heating rate, ΔH_{mI} grows at the expense of ΔH_{cII} and ΔH_{mII} , although the changes of T_{mI} and T_{mII} are difficult to detect. At lower crystallization temperature, the recrystallization is so active that double melting persists at heating rate 80°C/min. For samples crystallized at higher temperature, recrystallization in the subsequent scan is hindered at higher heating rates so that only a single melting endotherm appears.

Partial melting study further supports the postulation of melt-recrystallization. When crystallinity develops through the T_{cII} region, subsequent scans of partially melted samples indicates the continuous reorganization from where it was interrupted.

PLLA is prone to recrystallization. Melt-recrystallization of metastable crystals is believed to be the most probable origin of double melting in PLLA based on our observations. The occurrence of double melting depends largely on the perfection

of the original crystal after treatment, not the initial crystallinity, nor the completion of crystallization. In fact, judging the completion of crystallization from the disappearance of cold-crystallization peak, it seems even when the crystallization is not completed in some cases, as long as the crystals formed are more perfect and more stable, only a single melting peak was detected. In other cases, regardless of the completion of crystallization during the heating scan and relatively high crystallinity values, the crystals were small and ill-formed so that they would, by all means, experience reorganization during the subsequent heating and fail to show structure periodicity in SAXS. However, when samples are cold-crystallized at high temperature, dual lamellar population may exist in the samples and lead to the appearance of double melting peaks as well.

In WAXD patterns, a peak at $2\theta=24.5^\circ$ does not seem to develop as other reflections when the crystallization temperature increases and crystallinity rises. We thus do not exclude the possibility that a new crystal phase, δ , could have been mixed with the major α -phase and also contributes to the origin of double melting in PLLA, although the transition from δ -phase to α -phase at elevated temperature seems unlikely.

Finally, the estimated equilibrium melting temperature, T_m^0 , is $207\pm3^\circ\text{C}$ from both Gibbs-Thomson and Hoffman-Weeks equation, and is in agreement with existing literature. The equilibrium heat of fusion, ΔH_m^0 , of PLLA was determined from extrapolation of the heat of fusion versus specific volume to be 90 ± 4 J/g, which is consistent with the frequently quoted value, 93 J/g. This method seems to be a better

method for the estimation of ΔH_m^0 for PLLA, provided the 100% crystalline density is reliable. On the other hand, Flory method is rather questionable in the determination of these equilibrium values of PLLA.

CHAPTER 8 FUTURE RESEARCH

Current research has explored the double melting behavior of amorphous PLLA film and its possible origin, in terms of different crystallization conditions. A brief investigation of molecular weight effect was also conducted. In order to have a more thorough understanding of this phenomenon in PLLAs, studies can be extended to areas as follows.

1. A series of samples with similar molecular weight, but different polydispersity;
2. A series of samples with similar polydispersity, but different molecular weights;
3. A series of samples with similar molecular weight and polydispersity, but different levels of D-isomer content;
4. A series of uniaxially stretched film with different stretch temperatures and ratios;
5. A series of bi-axially stretched film with different stretch temperatures and ratios;
6. A series of as-spun fibers with different spinning parameters such as temperatures, take-up speeds and feed;
7. A series of drawn fibers with different draw ratios and temperatures.

As a result, one will acquire a better picture regarding the conditions that multiple melting would occur, the possible origins in connection with different forms (film, fiber, etc.).

LIST OF REFERENCES

1. D. Garlotta, "A literature review of poly(lactic acid)." *Journal of Polymers and the Environment* **9**(2), 63-84 (2002).
2. B. Linnemann, M. Sri Harwoko, and T. Gries, "Polylactide fibers (PLA)," *Chemical Fibers International* **53**(6), 426-433 (2003).
3. J. Randall, K. McCarthy, J. Krueger, P. Smith, and J. Spruiell, "Properties of polylactic acid optical copolymers achieved through stress induced crystallization," *Annual Technical Conference - Society of Plastics Engineers 58th*(Vol. 3), 3728-3730 (2000).
4. J. E. Spruiell, K. Mezghani, C. M. Ryan, D. Sawyer, A. Brosch, N. Buehler, and S. Gessner, "PLA - New material for non-wovens," *INDA-TEC 97, International Nonwovens Technical Conference, Book of Papers, Cambridge, Mass., Sept. 8-10, 1997*, 25.20-25.12 (1997).
5. M. W. Williams, "Processing and properties of high-speed melt spun and drawn poly(L-lactide) fibers.," (The University of Tennessee, Knoxville, Knoxville, 2001).
6. R. N. Holmes, "Development of bioabsorbable fiber-reinforced composites from bicomponent fibers of polylactic acid and its copolymers.," (The University of Tennessee, Knoxville, 2000).
7. X. Ling, "On the fine structure of poly(L-lactic acid) filaments," (The University of Tennessee, Knoxville, 2003).
8. K. Mezghani, M. W. Williams, and J. E. Spruiell, "Effect of molecular variables on structure development in high speed melt-spun polylactide filaments.," *Proceedings of the 17th Annual Meeting of Polymer Processing Society* (281-300)(2001).
9. S. Jacobsen, P. Degée, H. G. Fritz, P. Dubois, and R. Jérôme, "Polylactide (PLA) -- a new way of production.," *Polymer Engineering and Science* **39**(7), 1311-1319 (1999).
10. H. Tsuji, "Polylactides," *Biopolymers* **4**, 129-177 (2002).
11. P. DeSantis and A. J. Kovacs, "Molecular conformation of poly(S-lactic acid).," *Biopolymers* **6**(3), 299-306 (1968).
12. D. Brizzolara, H.-J. Cantow, K. Diederichs, E. Keller, and A. J. Domb, "Mechanism of the Stereocomplex Formation between Enantiomeric Poly(lactide)s.," *Macromolecules* **29**(1), 191-197 (1996).
13. J. Kobayashi, T. Asahi, M. Ichiki, A. Oikawa, H. Suzuki, T. Watanabe, E. Fukada, and Y. Shikinami, "Structure and optical properties of poly lactic acids.," *Journal of Applied Physics* **77**(7), 2957-2973 (1995).
14. C. Marega, A. Marigo, V. D. Noto, R. Zannetti, A. Martorana, and G. Paganetto, "Structure and crystallization kinetics of poly(L-lactic acid).," *Makromolekulare Chemie* **193**(7), 1599-1606 (1992).
15. T. Miyata and T. Masuko, "Morphology of poly(L-lactide) solution-grown crystals.," *Polymer* **38**(16), 4003-4009 (1997).
16. W. Hoogsteen, A. R. Postema, A. J. Pennings, G. t. Brinke, and P. Zugenmaier, "Crystal structure, conformation, and morphology of solution-spun poly(L-lactide) fibers.," *Macromolecules* **23**(2), 634-642 (1990).

17. B. Eling, S. Gogolewski, and A. J. Pennings, "Biodegradable materials of poly(L-lactic acid): 1. Melt-spun and solution-spun fibres.," *Polymer* **23**(11), 1587-1593 (1982).
18. J. Puiggali, Y. Ikada, H. Tsuji, L. Cartier, T. Okihara, and B. Lotz, "The frustrated structure of poly(L-lactide).," *Polymer* **41**(25), 8921-8930 (2000).
19. L. Cartier, T. Okihara, and B. Lotz, "Triangular polymer single crystals: stereocomplexes, twins, and frustrated structures.," *Macromolecules* **30**(20), 6313-6322 (1997).
20. L. Cartier, T. Okihara, Y. Ikada, H. Tsuji, J. Puiggali, and B. Lotz, "Epitaxial crystallization and crystalline polymorphism of polylactides.," *Polymer* **41**(25), 8909-8919 (2000).
21. S. Brochu, R. E. Prud'homme, I. Barakat, and R. Jerome, "Stereocomplexation and Morphology of Polylactides," *Macromolecules* **28**(15), 5230-5239 (1995).
22. Y. Ikada, K. Jamshidi, H. Tsuji, and S. H. Hyon, "Stereocomplex formation between enantiomeric poly(lactides)," *Macromolecules* **20**(4), 904-906 (1987).
23. T. Okihara, M. Tsuji, A. Kawaguchi, K. Katayama, H. Tsuji, S. H. Hyon, and Y. Ikada, "Crystal structure of stereocomplex of poly(L-lactide) and poly(D-lactide).," *Journal of Macromolecular Science, Physics* **30**(1-2), 119-140 (1991).
24. H. Tsuji, F. Horii, S. H. Hyon, and Y. Ikada, "Stereocomplex formation between enantiomeric poly(lactic acid)s. 2. Stereocomplex formation in concentrated solutions," *Macromolecules* **24**(10), 2719-2724 (1991).
25. H. Tsuji, S. H. Hyon, and Y. Ikada, "Stereocomplex formation between enantiomeric poly(lactic acid)s. 3. Calorimetric studies on blend films cast from dilute solution," *Macromolecules* **24**(20), 5651-5656 (1991).
26. H. Tsuji, S. H. Hyon, and Y. Ikada, "Stereocomplex formation between enantiomeric poly(lactic acid)s. 4. Differential scanning calorimetric studies on precipitates from mixed solutions of poly(D-lactic acid) and poly(L-lactic acid).," *Macromolecules* **24**(20), 5657-5662 (1991).
27. H. Tsuji, S. H. Hyon, and Y. Ikada, "Stereocomplex formation between enantiomeric poly(lactic acids). 5. Calorimetric and morphological studies on the stereocomplex formed in acetonitrile solution," *Macromolecules* **25**(11), 2940-2946 (1992).
28. H. Tsuji and Y. Ikada, "Stereocomplex formation between enantiomeric poly(lactic acid)s. 6. Binary blends from copolymers," *Macromolecules* **25**(21), 5719-5723 (1992).
29. H. Tsuji, F. Horii, M. Nakagawa, Y. Ikada, H. Odani, and R. Kitamaru, "Stereocomplex formation between enantiomeric poly(lactic acid)s. 7. Phase structure of the stereocomplex crystallized from a dilute acetonitrile solution as studied by high-resolution solid-state carbon-13 NMR spectroscopy," *Macromolecules* **25**(16), 4114-4118 (1992).
30. H. Tsuji, Y. Ikada, S. H. Hyon, Y. Kimura, and T. Kitao, "Stereocomplex formation between enantiomeric poly(lactic acid). VIII. Complex fibers spun from mixed solution of poly (D-lactic acid) and poly (L-lactic acid).," *Journal of Applied Polymer Science* **51**(2), 337-344 (1994).

31. H. Tsuji and Y. Ikada, "Stereocomplex formation between enantiomeric poly(lactic acids). 9. Stereocomplexation from the melt," *Macromolecules* **26**(25), 6918-6926 (1993).
32. B. Kalb and A. J. Pennings, "General crystallization behavior of poly(L-lactic acid)." *Polymer* **21**(6), 607-612 (1980).
33. R. Vasanthakumari and A. J. Pennings, "Crystallization kinetics of poly(lactic acid)." *Polymer* **24**(2), 175-178 (1983).
34. E. Urbanovici, H. A. Schneider, D. Brizzolara, and H. J. Cantow, "Isothermal melt crystallization kinetics of poly(L-lactic acid)." *Journal of Thermal Analysis* **47**(4), 931-939 (1996).
35. T. Miyata and T. Masuko, "Crystallization behaviour of poly(L-lactide)." *Polymer* **39**(22), 5515-5521 (1998).
36. S. Mazzullo, G. Paganetto, and A. Celli, "Regime III crystallization in poly(L-lactic acid)." *Progress in Colloid and Polymer Science* **87**(Solidification processes of polymers), 32-34 (1992).
37. M. L. D. Lorenzo, "Determination of spherulite growth rates of poly(L-lactic acid) using combined isothermal and non-isothermal procedures.," *Polymer* **42**(23), 9441-9446 (2001).
38. S. Iannace and L. Nicolais, "Isothermal crystallization and chain mobility of poly(L-lactide)." *Journal of Applied Polymer Science* **64**(5), 911-919 (1997).
39. J.-R. Sarasua, R. E. Prud'homme, and M. Wisniewski, "Crystallization and melting behavior of polylactides.," *Macromolecules* **31**(12), 3895-3905 (1998).
40. K. Jamshidi, S.-H. Hyon, and Y. Ikada, "Thermal characterization of polylactides.," *Polymer* **29**(12), 2229-2234 (1988).
41. D. M. Bigg, "Effect of copolymer ratio on the crystallinity and properties of polylactic acid copolymers," *Annual Technical Conference - Society of Plastics Engineers* **54th**(Vol. 2), 2028-2039 (1996).
42. P. Zhu and D. Ma, "Double cold crystallization peaks of poly(ethylene terephthalate)-1. Samples isothermally crystallized at low temperatures," *European Polymer Journal* **33**(10-12), 1817-1818 (1997).
43. P. Zhu and D. Ma, "Study on the double cold crystallization peaks of poly(ethylene terephthalate) (PET): 2. Samples isothermally crystallized at high temperature," *European Polymer Journal* **35**(4), 739-742 (1999).
44. Z. Pingping and M. Dezhu, "Study on the double cold crystallization peaks of poly(ethylene terephthalate) 3. The influence of the addition of calcium carbonate (CaCO₃)," *European Polymer Journal* **36**(11), 2471-2475 (2000).
45. S. X. Lu and P. Cebe, "Effects of annealing on the disappearance and creation of constrained amorphous phase," *Polymer* **37**(21), 4857-4863 (1996).
46. S. Yang, X. Chen, and Y. Chen, "Crystallinity of poly(ethylene terephthalate). IX. Nature of double peaks of cold crystallization," *Gaofenzi Tongxun* (3), 207-211 (1985).
47. J. E. Mark, *Polymer Data Handbook* (Oxford University Press, New York, Oxford, 1999).
48. I. A. M. Al Raheil, "Morphology and crystallization of poly(ethylene terephthalate)," *Polymer International* **35**(2), 189-195 (1994).

49. H. G. Kim and R. E. Robertson, "Multiple melting endotherms in isothermally melt-crystallized poly(butylene terephthalate)," *Journal of Polymer Science, Part B: Polymer Physics* **36**(10), 1757-1767 (1998).
50. J. S. Chung and P. Cebe, "Melting behavior of poly(phenylene sulfide). 2. Multiple-stage melt crystallization," *Polymer* **33**(11), 2325-2333 (1992).
51. P. Cebe, "Annealing study of poly(ether ether ketone)," *Journal of Materials Science* **23**(10), 3721-3731 (1988).
52. D. J. Blundell and B. N. Osborn, "The morphology of poly(aryl-ether-ether-ketone)," *Polymer* **24**(8), 953-958 (1983).
53. D. J. Blundell, "On the interpretation of multiple melting peaks in poly(ether ether ketone)," *Polymer* **28**(13), 2248-2251 (1987).
54. Y. Lee and R. S. Porter, "Double-melting behavior of poly(ether ether ketone)," *Macromolecules* **20**(6), 1336-1341 (1987).
55. Y. Lee, R. S. Porter, and J. S. Lin, "On the double-melting behavior of poly(ether ether ketone)," *Macromolecules* **22**(4), 1756-1760 (1989).
56. A. M. Jonas, T. P. Russell, and D. Y. Yoon, "Synchrotron X-ray Scattering Studies of Crystallization of Poly(ether-ether-ketone) from the Glass and Structural Changes during Subsequent Heating-Cooling Processes," *Macromolecules* **28**(25), 8491-8503 (1995).
57. C. Fournies, M. Dosiere, M. H. J. Koch, and J. Roovers, "Morphological study and melting behavior of narrow molecular weight fractions of poly(aryl ether ether ketone) (PEEK) annealed from the glassy state," *Macromolecules* **31**(18), 6266-6274 (1998).
58. C. Fournies, P. Damman, M. Dosiere, and M. H. J. Koch, "Time-Resolved SAXS, WAXS, and DSC Study of Melting of Poly(aryl ether ether ketone) (PEEK) Annealed from the Amorphous State," *Macromolecules* **30**(5), 1392-1399 (1997).
59. D. A. Ivanov, R. Legras, and A. M. Jonas, "The crystallization of poly(aryl-ether-ether-ketone) (PEEK): reorganization processes during gradual reheating of cold-crystallized samples," *Polymer* **41**(10), 3719-3727 (2000).
60. M. P. Lattimer, J. K. Hobbs, M. J. Hill, and P. J. Barham, "On the origin of the multiple endotherms in PEEK," *Polymer* **33**(18), 3971-3973 (1992).
61. J. Wang, M. Alvarez, W. Zhang, Z. Wu, Y. Li, and B. Chu, "Synchrotron small-angle x-ray scattering study of crystalline structures and isothermal crystallization kinetics of poly(aryl ether ether ketones)," *Macromolecules* **25**(25), 6943-6951 (1992).
62. K. N. Krueger and H. G. Zachmann, "Investigation of the melting behavior of poly(aryl ether ketones) by simultaneous measurements of SAXS and WAXS employing synchrotron radiation," *Macromolecules* **26**(19), 5202-5208 (1993).
63. Z. Zhang and H. Zeng, "Effects of thermal treatment on poly(ether ether ketone)," *Polymer* **34**(17), 3648-3652 (1993).
64. B. S. Hsiao, K. H. Gardner, D. Q. Wu, and B. Chu, "Time-resolved x-ray study of poly(aryl ether ether ketone) crystallization and melting behavior. 2. Melting," *Polymer* **34**(19), 3996-4003 (1993).

65. B. S. Hsiao, K. H. Gardner, D. Q. Wu, and B. Chu, "Time-resolved x-ray study of poly(aryl ether ether ketone) crystallization and melting behavior. 1. Crystallization," *Polymer* **34**(19), 3986-3995 (1993).
66. C. Bas, P. Battesti, and N. D. Alberola, "Crystallization and melting behaviors of poly(aryl ether ether ketone) (PEEK) on origin of double melting peaks," *Journal of Applied Polymer Science* **53**(13), 1745-1757 (1994).
67. C. Bas, A. C. Grillet, F. Thimon, and N. D. Alberola, "Crystallization kinetics of poly(aryl ether ether ketone): time-temperature-transformation and continuous-cooling-transformation diagrams," *European Polymer Journal* **31**(10), 911-921 (1995).
68. B. S. Hsiao, B. B. Sauer, R. K. Verma, H. G. Zachmann, S. Seifert, B. Chu, and P. Harney, "New Insight of Isothermal Melt Crystallization in Poly(aryl ether ether ketone) via Time-Resolved Simultaneous Small-Angle X-ray Scattering/Wide-Angle X-ray Diffraction Measurements," *Macromolecules* **28**(20), 6931-6936 (1995).
69. C. Y. Chen and E. M. Woo, "Some new evidence for polymorphism in cold-crystallized and melt-crystallized poly(ether ether ketone)," *Polymer Journal (Tokyo)* **27**(4), 361-370 (1995).
70. R. K. Verma, V. Velikov, R. G. Kander, H. Marand, B. Chu, and B. S. Hsiao, "SAXS studies of lamellar level morphological changes during crystallization and melting in PEEK," *Polymer* **37**(24), 5357-5365 (1996).
71. T. Y. Ko and E. M. Woo, "Changes and distribution of lamellae in the spherulites of poly(ether ether ketone) upon stepwise crystallization," *Polymer* **37**(7), 1167-1175 (1996).
72. R. Verma, H. Marand, and B. Hsiao, "Morphological Changes during Secondary Crystallization and Subsequent Melting In Poly(ether ether ketone) as Studied by Real Time Small Angle X-ray Scattering," *Macromolecules* **29**(24), 7767-7775 (1996).
73. S. Tan, A. Su, J. Luo, and E. Zhou, "Crystallization kinetics of poly(ether ether ketone) (PEEK) from its metastable melt," *Polymer* **40**(5), 1223-1231 (1998).
74. H. Marand, A. Alizadeh, R. Farmer, R. Desai, and V. Velikov, "Influence of Structural and Topological Constraints on the Crystallization and Melting Behavior of Polymers. 2. Poly(arylene ether ether ketone)," *Macromolecules* **33**(9), 3392-3403 (2000).
75. P. B. Rim and J. P. Runt, "Melting behavior of crystalline/compatible polymer blends: poly(ϵ -caprolactone)/poly(styrene-co-acrylonitrile)," *Macromolecules* **16**(5), 762-768 (1983).
76. C.-L. Wei, M. Chen, and F.-E. Yu, "Temperature modulated DSC and DSC studies on the origin of double melting peaks in poly(ether ether ketone)," *Polymer* **44**(26), 8185-8193 (2003).
77. S. Z. D. Cheng, M. Y. Cao, and B. Wunderlich, "Glass transition and melting behavior of poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK)," *Macromolecules* **19**(7), 1868-1876 (1986).
78. C. Fournies, P. Damman, D. Villers, M. Dosiere, and M. H. J. Koch, "Time-Resolved SAXS, WAXS, and DSC Study of the Annealing of Poly(aryl ether

- ether ketone) (PEEK) from the Glassy State," *Macromolecules* **30**(5), 1385-1391 (1997).
79. P. Cebe and S. D. Hong, "Crystallization behavior of poly(ether ether ketone)," *Polymer* **27**(8), 1183-1192 (1986).
 80. D. C. Bassett, R. H. Olley, and I. A. M. Al Raheil, "On crystallization phenomena in PEEK," *Polymer* **29**(10), 1745-1754 (1988).
 81. G. Groeninckx, H. Reynaers, H. Berghmans, and G. Smets, "Morphology and melting behavior of semicrystalline poly(ethylene terephthalate). I. Isothermally crystallized PET," *Journal of Polymer Science, Polymer Physics Edition* **18**(6), 1311-1324 (1980).
 82. J. Boon, G. Challa, and D. W. Van Krevelen, "Crystallization kinetics of isotactic polystyrene. I. Spherulitic growth rate," *Journal of Polymer Science, Polymer Physics Edition* **6**(10), 1791-1801 (1968).
 83. P. J. Lemstra, T. Kooistra, and G. Challa, "Melting behavior of isotactic polystyrene," *Journal of Polymer Science, Polymer Physics Edition* **10**(5), 823-833 (1972).
 84. P. J. Lemstra, A. J. Schouten, and G. Challa, "Secondary crystallization of isotactic polystyrene," *Journal of Polymer Science, Polymer Physics Edition* **12**(8), 1565-1574 (1974).
 85. T. Liu and J. Petermann, "Multiple melting behavior in isothermally cold-crystallized isotactic polystyrene," *Polymer* **42**(15), 6453-6461 (2001).
 86. T. Liu, "Melting behavior of isotactic polystyrene revealed by differential scanning calorimetry and transmission electron microscopy," *European Polymer Journal* **39**(7), 1311-1317 (2003).
 87. Y. Duan, J. Zhang, D. Shen, and S. Yan, "In Situ FTIR Studies on the Cold-Crystallization Process and Multiple Melting Behavior of Isotactic Polystyrene," *Macromolecules* **36**(13), 4874-4879 (2003).
 88. J. P. Bell and T. Murayama, "Relations between dynamic mechanical properties and melting behavior of nylon 66 and poly(ethylene terephthalate)," *Journal of Polymer Science, Polymer Physics Edition* **7**(6), 1059-1073 (1969).
 89. R. C. Roberts, "Poly(ethylene terephthalate). II. Morphological changes on annealing," *Polymer* **10**(2), 117-125 (1969).
 90. R. C. Roberts, "Melting behavior of bulk crystallized polymers," *Journal of Polymer Science, Polymer Letters Edition* **8**(5), 381-384 (1970).
 91. C. Zhou and S. B. Clough, "Multiple melting endotherms of poly(ethylene terephthalate)," *Polymer Engineering and Science* **28**(2), 65-68 (1988).
 92. A. M. A. Qudah and I. A. Al-Raheil, "Morphology and melting behavior of poly(ethylene terephthalate) crystallized from the glassy state," *Polymer International* **38**(4), 367-373 (1995).
 93. F. J. Medellin-Rodriguez, P. J. Phillips, J. A. Lin, and R. Campos, "The triple melting behavior of poly(ethylene terephthalate): molecular weight effects," *Journal of Polymer Science, Part B: Polymer Physics* **35**(11), 1757-1774 (1997).
 94. S. Y. Hobbs and C. F. Pratt, "Multiple melting in poly(butylene terephthalate)," *Polymer* **16**(6), 462-464 (1975).

95. A. M. A. Qudah and I. A. Al-Raheil, "Surface morphology and annealing of poly(butylene terephthalate)," *Polymer International* **38**(4), 375-380 (1995).
96. I. A. Al-Raheil, A. M. Qudah, and M. Al-Share, "Isotactic polypropylene crystallized from the melt. II. Thermal melting behavior," *Journal of Applied Polymer Science* **67**(7), 1267-1271 (1998).
97. M. Aboulfaraj, B. Ulrich, A. Dahoun, and C. G'Sell, "Spherulitic morphology of isotactic polypropylene investigated by scanning electron microscopy," *Polymer* **34**(23), 4817-4825 (1993).
98. P. Corradini, R. Napolitano, L. Oliva, V. Petraccone, B. Pirozzi, and G. Guerra, "A possible structural interpretation of the two DSC melting peaks of isotactic polypropylene in the α -modification," *Makromolekulare Chemie, Rapid Communications* **3**(10), 753-756 (1982).
99. C. De Rosa, G. Guerra, R. Napolitano, V. Petraccone, and B. Pirozzi, "Conditions for the α_1 - α_2 transition in isotactic polypropylene samples," *European Polymer Journal* **20**(10), 937-941 (1984).
100. G. Guerra, V. Petraccone, P. Corradini, C. De Rosa, R. Napolitano, and B. Pirozzi, "Crystalline order and melting behavior of isotactic polypropylene (α form)," *Journal of Polymer Science, Polymer Physics Edition* **22**(6), 1029-1039 (1984).
101. C. De Rosa, G. Guerra, R. Napolitano, V. Petraccone, and B. Pirozzi, "Crystalline order and melting behavior of isotactic polypropylene (α -form). III. Isothermally crystallized samples," *Journal of Thermal Analysis* **30**(6), 1331-1335 (1985).
102. V. Petraccone, C. De Rosa, G. Guerra, and A. Tuzi, "On the double peak shape of melting endotherms of isothermally crystallized isotactic polypropylene samples," *Makromolekulare Chemie, Rapid Communications* **5**(10), 631-634 (1984).
103. E. Martuscelli, M. Pracella, and L. Crispino, "Crystallization behavior of fractions of isotactic polypropylene with different degrees of stereoregularity," *Polymer* **24**(6), 693-699 (1983).
104. J. Weng, R. H. Olley, D. C. Bassett, and P. Jaaskelainen, "On morphology and multiple melting in polypropylene," *Journal of Macromolecular Science, Physics* **B41**(4-6), 891-908 (2002).
105. Y. S. Yadav and P. C. Jain, "Melting behavior of isotactic polypropylene isothermally crystallized from the melt," *Polymer* **27**(5), 721-727 (1986).
106. J. J. Janimak, S. Z. D. Cheng, A. Zhang, and E. T. Hsieh, "Isotacticity effect on crystallization and melting in polypropylene fractions. 3. Overall crystallization and melting behavior," *Polymer* **33**(4), 728-735 (1992).
107. J. J. Janimak, S. Z. D. Cheng, P. A. Giusti, and E. T. Hsieh, "Isotacticity effect on crystallization and melting in polypropylene fractions. II. Linear crystal growth rate and morphology study," *Macromolecules* **24**(9), 2253-2260 (1991).
108. X. Zhu, D. Yan, S. Tan, T. Wang, D. Yan, and E. Zhou, "Further study on double-melting endotherms of isotactic polypropylene," *Journal of Applied Polymer Science* **77**(1), 163-170 (2000).

109. J. Boor, Jr. and E. A. Youngman, "Preparation and characterization of syndiotactic polypropylene," *Journal of Polymer Science, Polymer Chemistry Edition* **4**(7), 1861-1884 (1966).
110. A. Marchetti and E. Martuscelli, "Effect of chain defects on the morphology and thermal behavior of solution-grown single crystals of syndiotactic polypropylene," *Journal of Polymer Science, Polymer Physics Edition* **12**(8), 1649-1666 (1974).
111. A. J. Lovinger, B. Lotz, and D. D. Davis, "Interchain packing and unit cell of syndiotactic polypropylene," *Polymer* **31**(12), 2253-2259 (1990).
112. G. Balbontin, D. Dainelli, M. Galimberti, and G. Paganetto, "Thermal behavior of highly stereoregular syndiotactic polypropylene from homogeneous catalysts," *Makromolekulare Chemie* **193**(3), 693-703 (1992).
113. J. Rodriguez-Arnold, A. Zhang, S. Z. D. Cheng, A. Lovinger, E. T. Hsieh, P. Chu, T. W. Johnson, K. G. Honnell, R. G. Geerts, and et al., "Crystallization, melting and morphology of syndiotactic polypropylene fractions: 1. Thermodynamic properties, overall crystallization and melting," *Polymer* **35**(9), 1884-1895 (1994).
114. P. Supaphol and J. E. Spruiell, "Thermal properties and isothermal crystallization of syndiotactic polypropylenes: differential scanning calorimetry and overall crystallization kinetics," *Journal of Applied Polymer Science* **75**(1), 44-59 (2000).
115. E. W. Fischer, H. J. Sterzel, and G. Wegner, "Investigation of the structure of solution grown of lactide copolymers by means of chemical reactions.," *Kolloid-Z. u. Z. Polymere* **251**(11), 980-990 (1973).
116. C. Migliaresi, D. Cohn, A. De Lollis, and L. Fambri, "Dynamic mechanical and calorimetric analysis of compression-molded poly(L-lactic acid) (PLLA) of different molecular weights: effect of thermal treatments," *Journal of Applied Polymer Science* **43**(1), 83-95 (1991).
117. C. Migliaresi, A. De Lollis, L. Fambri, and D. Cohn, "The effect of thermal history on the crystallinity of different molecular weight PLLA biodegradable polymers," *Clinical Materials* **8**(1-2), 111-118 (1991).
118. L. Fambri, A. Pegoretti, R. Fenner, S. D. Incardona, and C. Migliaresi, "Biodegradable fibres of poly(L-lactic acid) produced by melt spinning.," *Polymer* **38**(1), 79-85 (1997).
119. K. Mezghani and J. E. Spruiell, "High speed melt spinning of poly(L-lactic acid) filaments.," *Journal of Applied Polymer Science: Part B: Polymer Physics* **36**(6), 1005-1012 (1998).
120. J. K. Lee, K. H. Lee, and B. S. Jin, "Structure development and biodegradability of uniaxially stretched poly(L-lactide)," *European Polymer Journal* **37**(5), 907-914 (2001).
121. X. Yuan, A. F. T. Mak, K. W. Kwok, B. K. O. Yung, and K. Yao, "Characterization of poly(L-lactic acid) fibers produced by melt spinning," *Journal of Applied Polymer Science* **81**(1), 251-260 (2001).

122. M. Yasuniwa, S. Tsubakihara, Y. Sugimoto, and C. Nakafuku, "Thermal analysis of the double-melting behavior of poly(L-lactic acid)," *Journal of Polymer Science, Part B: Polymer Physics* **42**(1), 25-32 (2003).
123. Y. Ohtani, K. Okumura, and A. Kawaguchi, "Crystallization behavior of amorphous poly(L-Lactide)," *Journal of Macromolecular Science, Physics* **B42**(3 & 4), 875-888 (2003).
124. P. J. Flory, "Thermodynamics of crystallization in high polymers. IV. A theory of crystalline states and fusion in polymers, copolymers, and their mixtures with diluents.," *Journal of Chemical Physics* **17**, 223-240 (1949).
125. L. Mandelkern and P. J. Flory, "Melting and glassy-state transitions in cellulose esters and their mixtures with diluents," *Journal of the American Chemical Society* **73**, 3206-3212 (1951).
126. L. Mandelkern, R. R. Garrett, and P. J. Flory, "Heats of fusion of aliphatic polyesters," *Journal of the American Chemical Society* **74**, 3949-3951 (1952).
127. L. H. Sperling, *Introduction to physical polymer science*, 3rd Edition ed. (Wiley-Interscience, New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, 2001), pp. 217-243.
128. B. Wunderlich, *Macromolecular Physics, Vol. 3: Crystal Melting* (1980), p. 363 pp.
129. J. R. Isasi, L. Mandelkern, M. J. Galante, and R. G. Alamo, "The degree of crystallinity of monoclinic isotactic poly(propylene)," *Journal of Polymer Science, Part B: Polymer Physics* **37**(4), 323-334 (1999).
130. T. Sasaki, H. Sunago, and T. Hoshikawa, "Multiple melting behavior of syndiotactic 1,2-polybutadiene," *Polymer Engineering and Science* **43**(3), 629-638 (2003).
131. M. Pyda, A. Buzin, B. Wunderlich, and R. C. Bopp, "Morphology of poly(lactic acid) by AFM and calorimetry," *Proceedings of the NATAS Annual Conference on Thermal Analysis and Applications* **30th**, 463-468 (2002).
132. A. J. Nijenhuis, D. W. Grijpma, and A. J. Pennings, "Highly crystalline as-polymerized poly(L-lactide)," *Polymer Bulletin (Berlin, Germany)* **26**(1), 71-77 (1991).
133. J. F. Caron, (Laval University, 1996).
134. D. Cohn, H. Younes, and G. Marom, "Amorphous and crystalline morphologies in glycolic acid and lactic acid polymers," *Polymer* **28**(12), 2018-2022 (1987).
135. J. D. Hoffman and J. J. Weeks, "Melting process and equilibrium melting temperature of poly(chlorotrifluoroethylene)," *J. Research Natl. Bur. Standards* **66A**(1), 13-28 (1962).
136. M. Reading, "Modulated differential scanning calorimetry - a new way forward in materials characterization," *Trends in Polymer Science (Cambridge, United Kingdom)* **1**(8), 248-253 (1993).
137. J. M. Hutchinson, "Studying the glass transition by DSC and TMDSC," *Journal of Thermal Analysis and Calorimetry* **72**(2), 619-629 (2003).

138. M. Ribeiro and J. P. E. Grolier, "Temperature modulated DSC for the investigation of polymer materials. A brief account of recent studies," *Journal of Thermal Analysis and Calorimetry* **57**(1), 253-263 (1999).
139. C. Schick, "Temperature modulated differential scanning calorimetry (TMDSC) - basics and applications to polymers," *Handbook of Thermal Analysis and Calorimetry* **3**, 713-810 (2002).
140. S. L. Simon, "Temperature-modulated differential scanning calorimetry: theory and application," *Thermochimica Acta* **374**(1), 55-71 (2001).
141. B. Wunderlich, "The tribulations and successes on the road from DSC to TMDSC in the 20th century; the prospects for the 21st century," *Journal of Thermal Analysis and Calorimetry* **78**(1), 7-31 (2004).
142. J. F. Mano, Y. Wang, J. C. Viana, Z. Denchev, and M. J. Oliveira, "Cold crystallization of PLLA studied by simultaneous SAXS and WAXS," *Macromolecular Materials and Engineering* **289**(10), 910-915 (2004).
143. J. W. Leenslag and A. J. Pennings, "High-strength poly(L-lactide) fibers by a dry-spinning/hot-drawing process.," *Polymer* **28**(10), 1695-1702 (1987).
144. D. Sawai, K. Takahashi, T. Imamura, K. Nakamura, T. Kanamoto, and S.-H. Hyon, "Preparation of oriented b-form poly(L-lactic acid) by solid-state extrusion," *Journal of Polymer Science, Part B: Polymer Physics* **40**(1), 95-104 (2001).
145. R. Paukkeri and A. Lehtinen, "Thermal behavior of polypropylene fractions. 1. Influence of tacticity and molecular weight on crystallization and melting behavior," *Polymer* **34**(19), 4075-4082 (1993).
146. R. Paukkeri and A. Lehtinen, "Thermal behavior of polypropylene fractions. 2. The multiple melting peaks," *Polymer* **34**(19), 4083-4088 (1993).
147. M. Yasuniwa and T. Satou, "Multiple melting behavior of poly(butylene succinate). Part I. Thermal analysis of melt-crystallized samples," *Journal of Polymer Science, Part B: Polymer Physics* **40**(21), 2411-2420 (2002).

VITA

Xiaoyun Ling was born in Shanghai, China on November 7th, 1975. She went to Fudan University in Shanghai, where she received her Bachelor of Science degree in Polymer Materials and Engineering with a minor in Business Administration in July 1998. After graduation, she briefly worked for Tricon Global as a Manager Trainee. In the fall of 1999, she enrolled in the program of Polymer Engineering at the University of Tennessee, Knoxville. She received her Master and Doctorate degree in Polymer Engineering in August 2003 and December 2005, respectively. During the course, she took an internship at Ethicon Inc., a Johnson and Johnson company, in Summer 2002, where she participated in an exciting project of developing new generation biodegradable sutures.

Xiaoyun Ling married Kenneth M. Keilman on August 18th 2002 and they reside happily in a small town in New Jersey.