Non-isothermal Crystallization Kinetics, Multiple Melting Behaviors and Crystal Structure Simulation of Poly[(ethylene)-co-(trimethylene terephthalate)]s

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摘要

PET/PTT 共聚酯在熱差分析儀(Differential Scanning Calorimetry, DSC)中，以五種不同的冷卻速率(1~20°C/mim)來進行非等溫結晶。然後利用 Ozawa 與修改過的 Avrami 方程式分析共聚酯的非等溫結晶動力學。結果發現，除了組成為 66.3% trimethylene- (TT) and 33.7 % ethylene- terephthalates (ET)之共聚酯能夠符合 Ozawa 方程式。對於大部分共聚酯而言，無法利用 Ozawa 方程式分析來動力學。這是由於方程式本身的假設有不正確之處，例如不考慮二級結晶對非等溫結晶動力所造成的影響。若是以修改過的 Avrami 方程式分析的話，得知 Avrami 指數在 2.43 到 4.67 範圍之間，且與共聚酯的組成有關。此結果指出 PET/PTT 共聚酯在非等溫情況下，一級結晶為異質成核，三維空間球晶成長機構。不同的是，TT 或 ET 含量低於 10%以下共聚酯，我們發現到融熔溫度是關鍵的因素來決定是否可利用 Ozawa 方程式來分析非等溫結晶動力學。

在非等溫結晶中，不論共聚酯組成與冷卻速率為何，都只出現單一放熱峰。由此可判定在冷卻過程中，只產生單一型分佈球晶尺寸。非等溫結晶過後，利用 Temperature Modulated DSC (TMDSC)中的傳統(conventional)與調制(modulated)模式，來探討樣品的熔融行為。在兩種模式中皆可觀察出多重融熔峰。這些共聚酯的廣角 X 光繞射圖(Wide-angle X-ray Diffraction, WAXD)顯示出當結晶溫度增加時，繞射峰的強度會隨著增強，但所在之位置並不會有明顯的改變。它指出多重融熔峰並不是由於擁有不同的結晶結構的晶體發生融熔所造成的，因此可利用熔融再結晶模型來合理地解釋共聚酯的熔融行為。從 TMDSC 的可逆熱流以及不可逆熱流中，也能進一步地證實融熔-再結晶-再融熔的現象。此外，對於高 TT 含量之共聚酯，在可逆熱流上發現最高融熔溫度的一根小吸熱峰。它可合理地相信這是由於升溫過程中，在區域 I 所形成的結晶融熔所造成。

DSC 與 WAXD 用來研究 PET/PTT 共聚酯的共結晶(Cocrystallization)行為。在 DSC 熱曲線上，各種組成的共聚酯都可出現明顯的吸熱峰。含有 50% ET 的共聚酯具有最小融熔溫度。依照繞射峰位置，這些共聚酯的 WAXD 圖譜可區分成二大類，也就是 PET 與 PTT 型態的球晶。PET 與 PTT 型態間的結晶構造的轉移(Crystal transition)發生在由熔融溫度的變化量與組成所決定的共熔組成(50 % ET 和 TT)附近。此外，共熔組成的共聚酯，在 fiber diagram 與 WAXD 圖譜顯示出它具有不同結晶結構。這些結果指出 PET/PTT 共聚酯的共結晶行為是等向雙型態的(Isodimorphic)。
Abstract

Non-isothermal crystallization of the PET/PTT copolyesters was studied at five different cooling rates over 1-20°C/min by means of differential scanning calorimetry (DSC). Both the Ozawa equation and the modified Avrami equation have been used to analyze the crystallization kinetics. The non-isothermal kinetics of most copolymers cannot be described by the Ozawa analysis, except the copolyester with a composition of 66.3% trimethylene- (TT) and 33.7 %ethylene- terephthalates (ET). It may be due to the inaccuracy of the Ozawa assumptions, such as the secondary crystallization is neglected. From the kinetic analysis using the modified Avrami equation, the Avrami exponents, \( n \), were found to be in the range of 2.43-4.67 that are dependent on the composition of the copolyesters. The results indicated that the primary crystallization of the PET/PTT copolymers followed a heterogeneous nucleation and a spherulitic growth mechanism during the non-isothermal crystallization. In the cases of the copolyesters with either TT or ET less than 10%, we found the molten temperature is a key factor to decide whether the Ozawa equation can be succeeded in analyzing the dynamic crystallization.

For the non-isothermal crystallization, a single exothermic peak was detected in each DSC curve regardless of the composition and the cooling rate. It indicated that a single-mode distribution of the crystallite sizes was formed during the cooling process. After the non-isothermal crystallization, the melting behavior of the specimens was monitored by temperature modulated DSC (TMDSC) in the conventional mode and the modulated mode. Multiple endothermic peaks were observed in both modes. The wide-angle X-ray diffraction (WAXD) patterns of these copolymers showed that the peak height became sharper and sharper as the crystallization temperature increased, but the position of the diffraction peaks did not change apparently. It indicated that the
multiple melting behaviors did not originate from the melting of the crystals with different structures. The melting behavior of these PET/PTT copolyesters can be explained logically by using the melt-recrystallization model. From the reversing and non-reversing signals of TMDSC, the melting-recrystallization-remelting phenomena were further verified. In addition, a small endothermic peak was found at the highest melting temperature in the reversing thermogram for TT-enriched copolyesters. It is reasonably to believe that this endotherm is attributed to the melting of the crystals that are formed in regime I during the heating scan.

The cocrystallization of the PET/PTT copolyesters was studied using DSC and WAXD. A clear endothermic peak in the DSC thermogram was detected over the entire range of copolymer composition. A minimum melting temperature was found for the copolyester with 50% ET. The WAXD patterns of these copolymers can be divided into two groups with sharp diffraction peaks, i.e., PET type and PTT type crystals. The transition of crystal structure between PET type and PTT type occurred around the eutectic composition (50 % ET and TT), determined from the variation of the melting temperature with the composition. In addition, the fiber diagram and the WAXD pattern of the copolyester with the eutectic composition showed a different crystalline structure. These results indicated that the cocrystallization behavior of the PET/PTT copolyesters was isodimorphic.
1. Introduction

Poly(ethylene terephthalate) (PET) is a semicrystalline polymer with excellent thermal and mechanical properties, such as high chemical resistance and low gas permeability, etc. It is widely used in many aspects of life and industrial application, such as engineering plastic components, synthetic fiber, and packaging films. However, PET has some undesired properties, such as low moisture regain, poor dye ability, poor pilling, generation of static charge, poor adhesion to metal, and poor processing due to high melting temperature. Poly(trimethylene terephthalate) (PTT) is also a semicrystalline polymeric material, currently developed by Shell Chemical Corporation for fiber and engineering thermoplastic application. Both PET and PTT are belonged to the homologous series of the linear aromatic polyester, including poly (butylene terephthalate) (PBT). Chemical structures of PET and PTT are shown in Figures 1-1, and 1-2. PTT is an odd-numbered member of this homologous series. And it possesses better elastic recovery than PET and PBT. Because of the different number of methylene group along the backbone of these polyesters, the chain flexibility of PTT ought to be higher than PET, but lower than that of PBT. The melting point of PTT (233°C) is much lower than that of PET (265°C), and is nearly identical with that of PBT (232°C).\(^1\)

![Chemical structure of PET](Figure 1-1 Chemical structure of PET)
PET is a slow crystallizable material; however, PTT is able to crystallize fast and easily without adding nucleation agents. In general, copolymerization represents a way to modify morphology, melting point ($T_m$), glass transition temperature ($T_g$), crystallization rate, and the degree of crystallinity, etc. Most of the physical properties are strongly influenced by the composition and the arrangement of structural units in the chain.

Investigations of the crystallization kinetics of polymers are theoretically and practically significant. More frequently, the investigations are conducted under isothermal conditions because of the convenience of the theoretical treatment of the data. In practice, production and processing of polymers are often carried out under nonisothermal condition. Therefore, the study of the crystallization kinetics under dynamic condition is of great significance for the technological optimization and the manufacture of high performance polymeric materials. In the literatures, most groups investigated the dynamic crystallization kinetics of polymers by using Modified Avrami equation $^2$-$^5$ and Ozawa equation.$^7$

In fact, the melting behavior of crystallizable polymer is strongly depended on the morphological structure (size, shape, perfection, volume fraction, and orientation of crystallites) which was formed by crystallization from the molten state. The multiple melting behaviors of polymers crystallized from the melt have been investigated extensively. Three primary models have been proposed to explain this
behavior, \textit{i.e.}, simultaneous melting, recrystallization and remelting,\textsuperscript{23-41} melting of crystals with different lamellar thickness,\textsuperscript{42, 43} melting of different crystal structures.\textsuperscript{44} Both wide-angle X-ray diffraction (WAXD) measurements of powders and fibers are the fundamental methods for identifying the crystal structures of polymers. In addition, it is useful for us to understand and simulate the crystal structures and the parameters of these copolyesters by using molecular simulation software.

In this study, both the modified Avrami and Ozawa equations are used to analyze DSC data in order to know the non-isothermal crystallization kinetics of these PET/PTT copolyesters. Temperature modulated DSC (TMDSC) and conventional DSC are used to monitor the multiple melting endotherms of the copolyesters after dynamic crystallization at a different cooling rate ranging from 1 to 20\degree C/min. Regime I \(\rightarrow\) II transition temperatures \(T_{I \rightarrow II}\) of these copolyesters are estimated according to the DSC thermograms at a heating rate of 80\degree C/min. A diffractometer is used to investigate the WAXD patterns of these melt-crystallized copolyesters and the high temperature WAXD (HTWAXD) patterns of PTT enriched copolymers near \(T_{I \rightarrow II}\). Furthermore, the cocrystallization behavior is investigated using DSC and WAXD. Eventually, the crystalline structures and the parameters of these copolymers are investigated using fiber X-ray diffraction and molecular molding.
1.1. Objectives

- To study the nonisothermal crystallization kinetics of PET/PTT copolyesters by both modified Avrami equation and Ozawa method.
- To study the mechanism of the multiple melting behaviors of nonisothermal crystallized PET/PTT copolyesters as being revealed by TMDSC and conventional DSC techniques.
- To investigate the crystal structures and the parameters of these PET/PTT copolyesters by using various wide-angle X-ray diffraction methods.
- Try to simulate the crystalline structures of copolyesters by using Cerius² package software (version 4.6).

1.2. Flow Chart

![Flow Chart Image]

Figure 1-3 Schematic plot of the experimental flow chart
2. Paper review and theoretical background

2.1. Non-isothermal crystallization Kinetics

Traditional investigations for the crystallization kinetics of polymers were often limited to idealized conditions, because of the convenience of the theoretical treatment of the data. These studies led more understanding of the basic feature of polymer crystallization, but did not provide sufficient information for processing. In real situation, production and processing of crystallizable polymer are often carried out under non-isothermal condition, for example, melt-spinning, injection molding and extraction.

Majority of the proposed theoretical formulations for predicting non-isothermal crystallization kinetics is based on the modifications of Avrami equation.\textsuperscript{13,14}

A general form of Avrami equation is:

\[
1 - X_t = \exp(-kt^n)
\]

where \(X_t\) is the relative degree of crystallinity, the exponent \(n\) denotes a mechanism constant which value depends on the type of nucleation and the growth dimension, and the parameter \(k\) is a growth rate constant involving both nucleation and growth rate parameters.

Ziabicki proposed that the non-isothermal process could be viewed as a sequence of isothermal steps.\textsuperscript{15} The equation for the non-isothermal process is a series expansion of Avrami equation. Nakamura et al.\textsuperscript{16,17} suggested that by using the isothermal data a convenient procedure for the non-isothermal kinetics was based on the following assumption: the rate of crystallization at time \(t\) depended only on the temperature and the relative crystallinity at time \(t\), and it is independent of the
crystallization history.

A relative simple method to obtain the Avrami parameters from nonisothermal DSC experiments was developed by Ozawa. It is an extension of the theory of Evans for the isothermal crystallization. Ozawa took account of the effect of cooling rate on the dynamic crystallization, and extended the Avrami equation to the non-isothermal condition. Assuming that non-isothermal crystallization process may be composed of infinitesimally small isothermal crystallization steps, and the degree of conversion at temperature \( T, X_T \), can be written as eq. (2), according to the Ozawa equation,

\[
1 - X_T = \exp\left[-\frac{F(T)}{R^m}\right]
\]

where \( R \) is the cooling rate, \( X_T \) represents the relative crystallinity at temperature \( T \), \( F(T) \) is the cooling crystallization function of the process, and it is related to the overall crystallization, and how fast crystallization occurs, and \( m \) denotes the Ozawa exponent, having a value between 1 and 4 which depends on whether nucleation is instantaneous or sporadic and the dimension of crystal growth. Taking the logarithm of eq. (2) twice yields eq. (3).

\[
\log[-\ln(1 - X_T)] = \log F(T) + m \log R
\]

According to the Ozawa analysis, at a chosen temperature the relative crystallinities at different cooling rates should yield a straight line by plotting \( \log[-\ln(1 - X_T)] \) versus \( \log R \). This plot gives a series of parallel lines at different temperatures, as shown in Figure 2-1. The parameters, \( \log F(T) \) and \( m \), can be derived from the intercept and the slope, respectively. Two factors were ignored in the derivation of eq. (2). First, the slow secondary crystallization was not considered. This
could reduce the determined values of the Avrami parameters. However, the secondary crystallization would be virtually nonexistent as the temperature decreased under the dynamic crystallization condition. Another factor neglected in eq. (2) is the change of the folding length of polymer chain, which is a function of crystallization temperature. If the folded length decreases with a decrease in the crystallization temperature under non-isothermal crystallization, this factor should not be neglected in the derivation of eq. (2).

Ozawa\textsuperscript{7} investigated the nonisothermal crystallization of PET, and found that PET followed eq. (2). The $m$ values indicated that the crystallization was considered to proceed by randomly formed nuclei in three-dimension growth. These results were in agreement with those obtained isothermally. PTT\textsuperscript{4} also followed the Ozawa analysis over the cooling rates ranging from 0.63$^\circ$C/min to 20$^\circ$C/min. The mean value of the Ozawa exponent varied from 2.3 to 2.6 as the number-average molecular weight changed from 13,000 to 67,000. Eder and Wlochowicz conducted the dynamic crystallization of polypropylene,\textsuperscript{8} and expressed the cooling crystallization function as an exponential function of temperature. Except for PET, PTT and PP, many authors have successfully investigated the non-isothermal crystallization of many polymers by using Ozawa analysis, such as poly (ethylene isophthalate-co-terephthalate),\textsuperscript{3} poly(ethylene oxide) [PEO],\textsuperscript{5} and poly($p$-phenylene sulphide) [PPS].\textsuperscript{12} In another way, the non-linearity of Ozawa plot was observed in the case of polyethylene,\textsuperscript{8} PEEK,\textsuperscript{9} PEEKK,\textsuperscript{10} and poly(arylene ether ether sulfide).\textsuperscript{11} Eder and Wlochowicz \textsuperscript{8} addressed that the dynamic crystallization of polyethylene can not followed by Ozawa equation. It may be due to the factors that are neglected in the Ozawa equation, such as secondary crystallization, the dependence of lamellar thickness on crystallization temperature, and the occurrence of both sporadic and predetermined nucleation.
In bibliography, a modified Avrami equation\(^2\)\(^-\)\(^5\) was also frequently used to describe the non-isothermal crystallization process, by applying the Avrami equation to analyze the data obtained from the non-isothermal crystallization thermogram. During the dynamic crystallization process, the relative crystallinity \(X_T\) is a function of the crystallization temperature.

\[
X_T = \frac{\int_{T_o}^{T_c} \left( \frac{dH}{dT} \right) dT}{\int_{T_o}^{T_\infty} \left( \frac{dH}{dT} \right) dT}
\]  \hspace{1cm} (4)

Where \(T\) is the crystallization temperature at time \(t\), \(T_o\) and \(T_\infty\) are the initial and the end temperatures of dynamic crystallization, respectively. The relationship between the crystallization time \(t\) and the temperature \(T\) is given by:

\[
t = \frac{T_o - T}{R}
\]  \hspace{1cm} (5)

Using the double-logarithmic form of \(Eq. (1)\), and plotting \(\log[-\ln(1-X_T)]\) vs. \(\log t\) for each cooling rate, a straight line could be obtained because the modified Avrami analysis is valid for primary crystallization, as depicted in Figure 2-2. The parameters, \(k\) and \(n\), can be acquired from the intercept and the slope of the plot, respectively. It must be kept in mind that the values of \(k\) and \(n\) obtained from the non-isothermal crystallization do not have the same physical meanings as those obtained from the isothermal crystallization. The reason is due to the fact that the temperature changes continuously under the non-isothermal condition. This affects the rates of both nuclei formation and spherulite growth owing to they are temperature dependent. Jeziorny\(^18\) pointed out the parameter value of the rate constant, \(k\), should be corrected for the rate of crystallization, which depended on the cooling rate employed.
Furthermore, the half time of crystallization, $t_{1/2}$, is defined as the time to reach 50% of the relative crystallinity. It can be obtained by correcting with the crystallization rate constant $k'$, as shown in eq. (7).

$$t_{1/2} = \left( \frac{\ln 2}{k'} \right)^{1/n}$$

(7)

2.2. Thermal analysis

2.2.1. Differential scanning calorimeter (DSC)

DSC, a traditional instrument for thermal analysis of materials (polymer, inorganic and organic materials), has been used for four decades to measure the temperature and the heat flows along with the transitions in materials as a function of time or temperature. These measurements have provided useful information about physical and chemical changes that involve endothermic and exothermic processes or changes in the heat capacity.

2.2.2. Temperature modulated differential scanning calorimeter (TMDSC)

TMDSC is a relatively new technique. A specimen is subjected to a linear heating ramp, as in a standard DSC, and a superimposed low frequency temperature oscillation (modulation). A modulation in the heating profile is activated. As a result, TMDSC thermal analysis could provide the “total” heat flow - as the conventional DSC, and the heat capacity-related (reversible) component of the heat flow. The difference between the total and the reversing heat flow yields the non-reversing (NR) component. The mathematical equation representing TMDSC heat flow can be expressed as

$$\log k' = \frac{\log k}{R}$$

(6)
\[
\frac{dQ}{dt} = \beta C_v + f(t, T)
\]

where \( \frac{dQ}{dt} \) = total heat flow
\( \beta C_v \) = reversing heat flow
\( f(t, T) \) = non-reversing heat flow

The reversing heat flow of TMDSC, well known in the literature, is excellent for quantifying the glass transition because it separates the glass transition completely from other non-reversing processes, such as enthalpy relaxation and crystallization. Exothermic events are detected only in the non-reversing signal and absented from the reversing signals. Unfortunately, endothermic melting behavior can contribute to both reversing and NR signal and the relative fractions depend on the types of crystals present and the experimental conditions.

### 2.2.3. Interpretation of TMDSC\(^{27}\)

1. The non-reversing endothermic signal is typically due to complete melting of separate lamellae or stacks of lamellae.\(^{21, 28}\) In certain cases, perfected crystals with melting points are far away from their equilibrium melting point, and the crystals can not recrystallize fast enough because of a low degree of under cooling.

2. The reversing endothermic signal is due to partial melting of lamellae. They can rapidly recrystallize due to the template of the just melted chains, \( i.e. \), they can recrystallize on the existing crystals.\(^{21}\) The recrystallization occurs even though there is no local “cooling” in the temperature-modulated profile due of the small modulation amplitude relative to the underlying heating rate.

3. Crystallization exotherm only contributes to the non-reversing signal, making TMDSC a very powerful technique for separation of the exotherms from glass transition, reversible melting, or other heat capacity related events. Unfortunately,
exothermic and endothermic non-reversible events can occur simultaneously, and they are not completely resolved from each other. Since they can offset one another, one must be cautious while interpreting and comparing their magnitudes. Recognition of this explains why standard DSC and TMDSC are difficult to interpret for many polymers.\textsuperscript{21}

2.3. Multiple endotherm behaviors

When semicrystalline polymers crystallized isothermally or nonisothermally from the molten state, or annealed for an enough time, the DSC heating thermogram often exhibits two or more endothermic melting peaks. It was reported that the origin of multiple melting endotherms can be classified into three primary mechanisms, \textit{i.e.}, simultaneous-melting, recrystallization, and remelting (melt-recrystallization model),\textsuperscript{23-41} melting of different crystal structures,\textsuperscript{44} and melting of lamellae with different thickness (two morphologies).\textsuperscript{42,43} These mechanisms are briefly described as below.

First, the melting-recrystallization model proposed that polymer crystals are metastable, so they can proceed as a succession of melting-recrystallized-remelting under the heating scan. Three endothermic peaks appear to be a typical d.s.c. thermogram in a heating scan. The high-temperature melting peak is related to the primary lamellae which originated at the initial state, \textit{i.e.} primary crystallization. The minor low-temperature one is attributed to the melting of crystals formed during secondary crystallization. Generally speaking, imperfect crystals or lamellae melt at first and followed by recrystallization to form more thicker and/or perfected crystals during the heating scan. Figure 2-3 shows a typical heating thermogram of an annealed PET. Zhou and Clough\textsuperscript{29} suggested that this multiple melting behavior results from melting re-crystallization mechanism. Similar situation is also observed from semicrystalline polymers, such as syndiotactic polystyrene,\textsuperscript{24} poly(butylene terephthalate),\textsuperscript{31} poly
(ethylene-co-butylene naphthalene-2,6-dicarboxylate)s,\textsuperscript{35} poly(butylene isophthalate)\textsuperscript{36},
and poly(ethylene terethphalate-co-isophthalate).\textsuperscript{39}

Secondly, the dual morphology suggests that the different melting temperature
peaks are attributed to two different thick lamellae, \textit{i.e.}, the crystals are formed by
primary and secondary crystallization, respectively, but they have the same crystalline
structure. Stein and Mirsa\textsuperscript{41} reported the dual morphology of usual and unusual
spherulites in PBT. They stated that two endothermic peaks arose from the melting of
these two types of spherulites.

Thirdly, another mechanism suggests multiple melting endotherms phenomena
are caused by melting of the crystals that have different crystal structures. Prest\textsuperscript{44} \textit{et al.}
proposed that the multiple melting behavior of poly(vinylidene fluoride) resulted from
the melting of several crystal phases which possess different crystalline structures.

\textbf{2.4. Cocrystallization behavior of copolymer}

Some copolymers with both A/B components are crystallizable, and the degree of
crystallinity in general gradually decreases as the minor component increases. In some
cases, copolymers might become fully amorphous materials even at a low comonomer
composition. This is due to the incompatibility in crystal lattices of two components. In
literature, only a few systems including poly(3-hydroxybutyrate-co-3-hydroxyvalerate),
\textsuperscript{54-56} poly(hexamethylene terephthalate-co-hexamethylene 2,6-naphthalate),\textsuperscript{57} and poly
(butylene terephthalate-co-butylene 2,6-naphthalate)\textsuperscript{58} have been reported to compatible
in crystal lattices, \textit{i.e.} cocrystallization is testified by the presence of a clear melting
temperature and some crystallinity over the entire copolymer composition.
Cocrystallization behavior in A/B random copolyester can be divided into two groups,
\textit{i.e.}, isomorphism and isodimorphism. Generally speaking, if two components possess
the similar chemical structure, they should occupy approximately the same volume, and
the excess free energy of cocrystallization is very small, and therefore the chain
conformation of both corresponding homopolymers becomes compatible with entire
crystal lattice. As a result, only one crystalline phase containing both comonomer units
is detected over all composition, called isomorphism. In other words, copolymers may
show isodimorphism where two crystalline phase, each of which contains comonomer
units as a minor component are observed. In isodimorphism, the increase of minor
comonomer content in each crystalline phase is accompanied by lowering of melting
temperature and the crystallinity. Hence, a eutectic melting temperature is observed in
the plot of \( T_m \) versus copolymer composition. Lee et al.\(^{58}\) have reported that
poly(butylene terephthalate-\textit{co}-butylene 2,6-naphthalate) random copolyesters exhibit
isodimorphic cocrystallization behavior, and have verified the presence of a eutectic
melting temperature. The systematization can be divided into two types (PBT type and
PBN type) of wide-angle diffraction pattern. A similar situation is also observed in the
case of poly(hexamethylene terephthalate-\textit{co}-hexamethylene 2,6-naphthalate).\(^{57}\)

2.5. Crystal structures of polyester

Poulin-Dandurand et al.\(^{50}\) investigated the solution grown PTT crystals by using
wide-angle X-ray diffraction and electron diffraction (ED) pattern from transmission
electron microscope (TEM). They reported that PTT belonged to the triclinic system.

\[
\begin{align*}
 a &= 4.637 \text{ Å} \\
 b &= 6.266 \text{ Å} \\
 c &= 18.64 \text{ Å} \\
 \alpha &= 98.4^\circ \\
 \beta &= 93.0^\circ \\
 \gamma &= 111.1^\circ
\end{align*}
\]

In accordance with the cell parameters, the calculated crystal density is
1.387g/cm\(^3\), space group is P1, and the \(-\text{O-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}\) unit is in a
trans-gauche-gauche-trans conformation
Desborough et al.\textsuperscript{51} used WAXD to analyze PTT fibers, a triclinic unit cell was reported with

\[ a = 4.6 \text{ Å} \quad b = 6.2 \text{ Å} \quad c = 18.3 \text{ Å} \]

\[ \alpha = 98.0^\circ \quad \beta = 90.0^\circ \quad \gamma = 112^\circ \]

The calculated density is consistent with the measured density (1.43g/cm\textsuperscript{3}).

PET single crystal was analyzed by WAXD measurement.\textsuperscript{54} The unit cell of PET single crystal is identified to be triclinic.

\[ a = 4.48 \text{ Å} \quad b = 5.85 \text{ Å} \quad c = 10.75 \text{ Å} \]

\[ \alpha = 99.5^\circ \quad \beta = 118.4^\circ \quad \gamma = 112.2^\circ \]

So far, the crystalline structures of the PET/PTT copolymesters have not been reported in literature from our knowledge.

Figure 2-1 Typical Ozawa plots [7].
Figure 2-2 Typical modified Avrami plots [4].

Figure 2-3 Typical multiple endothermic peaks on heating process [29].
3. Experimental

3.1. Materials

Nine developmental grade samples were supplied by the Union Chemical Laboratories of Industrial Technology Research Institute (ITRI). They include PET, PTT homopolymers and their copolyesters. Table 1 lists the sample code and the composition of C2~C8. C1 and C9 represent PTT and PET homopolymers, respectively.

3.2. Instruments

Differential Scanning Calorimeter (DSC) Perkin-Elmer Pyris 1 DSC
Temperature Modulated Differential Scanning Calorimeter (TMDSC) TA Q100
Diffractometer Siemens D5000
Enraf-Nonius X-ray camera system Diffractis 582
Cerius² software (version 4.6) Molecular Simulation Inc.
Hot press machine Hung Ta Co., Ltd
Vacuum oven Schellab model 1410
Refrigerated vapor traps Savant model RVT 100

3.3. Sample preparation

PET/PTT copolyester pellets were sandwiched between two polyimide films and two copper plates. They were put in a hot press machine. During the molding process, pressure up to 8~10 kg/cm² was applied to get films. Both pellets and films were dried at 45°C in a vacuum oven for 12 hrs to remove moisture before using.
3.4. Temperature Modulated Differential Scanning Calorimeter (TMDSC)

For TMDSC and conventional DSC measurements, a TA instrument Q100 was used to investigate the non-isothermal crystallization and the melting behaviors of PET/PTT copolyesters.

3.4.1. Non-isothermal crystallization

Non-isothermal crystallization was performed under dry nitrogen atmosphere to avoid the oxidative degradation. Both temperature and heat flow were calibrated by indium standard. In this study, sample weight of 3-5 mg was used to minimize the effect of low thermal conductivity of polymers. Each sample was heated up to its molten temperature, \(^{45,46}\) as listed in the last column of Table 2, with a heating rate of 20\(^{\circ}\)C/min and then hold at that temperature for 5 min to remove thermal history. Then it was cooled to RT at one of five cooling rates ranging from 1 to 20\(^{\circ}\)C/min. Crystallization peak temperature (\(T_p\)), \(i.e.,\) the peak maximum of DSC thermogram and the heat of crystallization (\(\Delta H_c\)) were obtained from the DSC cooling curve. The exothermic heat of crystallization was analyzed by using modified Avrami equation (Jeziorny expression) and/or Ozawa equation.

3.4.2. Melting behaviors

For the TMDSC measurement, heat capacity calibration was carried out using a standard sapphire sample. Both the temperature and baseline were calibrated at a heating rate of 2 or 3\(^{\circ}\)C/min under nitrogen atmosphere by using Indium standard. The cell constant calibration was also performed with an Indium standard. Nonisothermal-crystallized samples were heated at a rate of 2 or 3\(^{\circ}\)C/min with an oscillation amplitude 0.212\(^{\circ}\)C or 0.318\(^{\circ}\)C and an oscillation period of 40 s. In addition, some samples were also heated at a rate of 50\(^{\circ}\)C/min to obtain multiple endothermic
peaks under conventional DSC condition.

3.5. Differential scanning calorimeter (DSC)

3.5.1. Specimens preparation for WAXD measurement

Perkin-Elmer Pyris 1 DSC was used to prepare specimens for WAXD measurements. The sample was heated to a predetermined melting condition (as listed in column 5 of Table II) and held for 5 min, in order to eliminate thermal history. After this pretreatment, the specimen was cooled down to a selected crystallization temperature at a fast cooling rate and then crystallized isothermally for 6~12 times of the crystallization peak time to ensure the isothermal crystallization completely.

3.5.2. Finding Regime I $\rightarrow$ II transition temperature ($T_{I\rightarrowII}$)

Specimen was heated to a melting condition (as listed in Table II) at a rate of 10°C/min and maintained for 5 min to remove the residual nuclei. Subsequently, it was cooled to a preset crystallization temperature at a rapid cooling rate and crystallized isothermally for 3~5 times of the total DSC crystallization time to ensure crystallization completely. Then the melt-crystallized PET/PTT copolyester was heated at a heating rate of 80°C/min to the melting state to observe the variation of endothermic peaks.

3.6. Wide-angle X-ray diffraction (WAXD) measurement

The X-ray analysis of the melt-crystallized samples was carried out at room temperature with a diffractometer (D5000, Siemens) in powder form. CuK$_\alpha$ radiation was employed as a radiation source ($\lambda=0.1542$ nm, 30 mA, 40 KV). The X-ray beam was mono-chromatized while using a graphite crystal. The scan range of 2θ angle was between 8° and 38°. Steps of 0.05° and 3 seconds per step were used throughout the
experiments.

3.7. High Temperature Wide-angle X-ray diffraction (HTWAXD) measurement

The dried PET/PTT copolyester pellets were dissolved in a mixture of 1,1,2,2-tetrachloroethane and phenol (2:3 w/w). A few drops of the solution were put and dried on the platinum plate, and heated from RT to $T_{I-II}$ at 10°C/min. It was then heated up to the molten temperature at a lower rate without melt flow. Cooled the specimen to a temperature in regime I, and monitored the variation of the diffraction pattern during isothermal crystallization.

3.8. Uniaxially Oriented Samples Preparation

The dried PET/PTT copolyester pellets were heated on a hot stage from RT to an applicable melting temperature, i.e., to remain in the molten state without flow. Subsequently, quick drew the melt during cooling to room temperature, and followed by further elongation. In order to keep the fiber orientation, the annealing temperature of monofilament is selected carefully. Then the heat treatments of these oriented PET/PTT copolymer fibers were carried out under tension in a vacuum oven for several days at the given temperature. The melting and annealing temperatures are tabulated in Table 23.

3.9. Fiber pattern measurement

Fiber patterns of wide-angle X-ray diffraction were obtained on flat imaging plate (12.5 cm × 12.5 cm) in camera using Ni-filtered copper radiation (wavelength = 1.5418 Å, 15 mA, 25 KV). The distance between the detector and sample is 7 cm. The collimator is used to produce the parallel beams.
4. Results and Discussion

4.1 Regime I → II transition temperature

C2 copolyester samples were heated up to 245°C at the rate of 10°C/min and then held for 5 min to erase the thermal history. After the pretreatment, they were cooled down to the given crystallization temperature ranging from 180 to 213°C at a rapid cooling rate, and were crystallized isothermally for 3~5 times of the total DSC crystallization time to ensure crystallization completely. These isothermal-crystallized specimens were heated at a rate of 80°C/min. The DSC thermograms exhibit multiple melting behaviors, as shown in Figures 1 and 2. It is obviously that the low melting peak shifts to high temperature, and gradually merges with the middle endothermic peak as the crystallization temperature increases. A single peak appears when the isothermal crystallization temperature is 198°C. While the crystallization temperature continuously increases to 210 or 213°C, the single melting peak is splits into two again. It is believed that the isothermal crystallization was complete because no exothermic signal was detected after enough time of isothermal crystallization. Hence, the smaller endothermic peak should not be regarded as the melting of the crystals which were formed during the cooling process. A similar situation has been reported by Huang, and he concluded that the Regime I → II transition temperature ($T_{I\rightarrow II}$) of PTT is about 215°C, based on the reference. As mention above, it is reasonable to believe that there are some regime I crystals formed isothermally at 210 and 213°C.

On the other side, the HTWAXD pattern for the specimen crystallized at 212°C (see Figure 16) shows only a sharp diffraction peak that is due to the diffraction of the (010) crystal plane. This diffraction pattern is quite different from those of C2 copolymer crystallized at a temperature ranging from 180 to 207°C, as shown in the
Figures 14 and 15. In this study, the crystals formed in Regime I (closed to the equilibrium temperature) may be not spherulities, but are axialites. It may be the reason why the HTWAXD patterns do not have complete diffraction peaks, which are induced by various crystal planes. Based on the reference, the existence of $T_{I\rightarrow II}$ was also detected by PLM study and the plot of $(T_m - T_c)$ versus log$t$. Similar melting behaviors were also observed at a heating rate of 80°C/min for C3, C4 and C8 copolyesters, as shown in Figures 17, 18, 31, 32, 67 and 68. The HTWAXD patterns of C3 and C4 copolyesters are plotted in Figures 19 and 33, respectively. The Regime I $\rightarrow$ II transition temperatures ($T_{I\rightarrow II}$) of C3, C4 and C8 are listed in column 11 of Table 3.

4.2 Non-isothermal crystallization

Nonisothermal crystallization was performed by TMDSC in the conventional mode with various cooling rates over 1-20°C/min from the molten state. These PET/PTT copolyesters revealed the typical crystallization exotherms as observed for common crystallizable polymers. A single exothermic peak is detected regardless of the cooling rate (see Figures 3, 19, 33, 46, 57, and 70). The peak height and the total area of an exothermic peak seem to increase with the cooling rate. This is due to the heat flow is defined as the exothermic heat per unit time. When the cooling rate increases, the exothermic peak becomes broader and shifts to the low temperature region, regardless of its composition. The peak crystallization temperature ($T_p$), the onset crystallization temperature ($T_{on}$), the differences between $T_{on}$ and $T_p$ ($\Delta T_1 = T_{on} - T_p$), and the enthalpy of crystallization ($\Delta H_c$) are tabulated in columns 2-3, 5-6 of Table 3. It is found that $T_{on}$, $T_p$, and $\Delta H_c$ decreased as the cooling rate increased. It is obvious when the crystals are formed at large supercooling, the polymer has no time to form perfect lamellae or crystals so that it possess lower enthalpy of crystallization.
The difference between $T_{on}$ and $T_p$ is often used to evaluate the overall crystallization rate of polymer in the dynamic crystallization. The larger the $T_{on} - T_p$ is, the smaller the rate of crystallization is. By referring to the sixth column of Table 3, the values of $\Delta T_1$ at a cooling rate of 1°C/min indicate the overall crystallization rate decreases in the order of C2 > C6 > C7 > C4 > C3 > C8. Regardless of the composition and the cooling rate, the relative crystallinity, $X_T$, increases exponentially with decreasing temperature and finally levels off, as shown in Figures 4, 20, 34, 47, 58 and 71. The plots of $X_T$ versus time are shown in Figures 5, 21, 35, 48, 59 and 72. It indicates the time required for complete crystallization increases when the cooling rate decreases.

4.2.1 Ozawa analysis

Non-isothermal crystallization from the melt at different cooling rates can be analyzed using the Ozawa approach. For instance, in the case of C2 PET/PTT copolyester, the results of Ozawa analysis are shown in Figure 6, by plotting log[-ln(1-$X_T$)] versus log$R$, for temperatures in the range from 174°C to 190°C. If the non-isothermal crystallization could be described by the Ozawa equation, the plots of log[-ln(1-$X_T$)] vs. log$R$ would give a series of parallel lines. The cooling function $F(T)$ and the Ozawa exponent $m$ can be calculated from the slope and the intercept, respectively. However, the curvature in Figure 6 indicated the dynamic crystallization of C2 copolyester did not follow the Ozawa equation. Similar results were also observed in PE, PEEK, PEEKK and Poly(arylene ether ether sulfide). One possible reason is due to the inaccurate assumptions in the Ozawa equation, such as secondary crystallization was neglected, the lamellar thickness depended on the crystallization temperature, and the cooling function $F(T)$ was not constant over the entire crystallization. Avrami exponent $n$ was also found to comply with the variation of crystallization temperature. In general, the dynamic crystallization
involves both primary and secondary crystallization, but Ozawa analysis neglects the existence of secondary crystallization. This phenomenon can be illustrated by plotting a vertical line at 190°C in Figure 4, the relative crystallinity ($X_T$) for the cooling rate at 10°C/min is very low, and the dynamic crystallization is in the initial stage. Whereas $X_T$ at 2°C/min is nearly 100%, the dynamic crystallization approaches its final stage. The crystallization kinetics should not be the same at different degrees of crystallinity, however, this factor is not considered in the Ozawa Analysis. Similar plots are observed in Figures 36, 49, 60 and 73, which reveal these copolyesters do not follow the Ozawa equation, except C3. For the temperature ranging from 141 to 150°C, the copolyester C3 shows a series of parallel lines, as previously reported in the literature. 3-5,7,12 The values of $m$ and log$F(T)$ are listed in Table 6. The Ozawa exponent, $m$, decreases from 3.24 to 2.68, and the logarithmic cooling function log$F(T)$ increases from 1.01 to 5.35, as the temperature decreases from 150 to 141°C. It suggests that the mechanism of this non-isothermal crystallization is a predetermined nucleation with three-dimensional growth.

**4.2.2 Analysis using modified Avrami equation**

As mentioned above, the non-isothermal crystallization kinetics of most copolyesters does not fit the Ozawa equation. Hence another analytical method, the modified Avrami equation, is used to analyze the non-isothermal data. In general, the Avrami plot usually shows an inflection issue, representing two different crystallization rates during the whole crystallization process. The initial stage of crystallization, or called primary crystallization, has a faster crystallization rate. In contrast, when crystallization reaches the later stage, the crystallization rate is slowed down due to spherulitic impingement and it is called secondary crystallization. The modified Avrami analysis is valid for primary crystallization, i.e., the crystallization at
the early stage. Typical Avrami plots are shown in Figures 9, 23, 37, 50, 61 and 76 by plotting \( \log[-\ln(1-X_t)] \) versus \( \log t \) at different cooling rates (1-20°C/min). Avrami parameters \( k \) and \( n \) are estimated from the slope and the interception of the plots. According to eq. 6 the crystallization rate constant \( k \) is corrected to obtain \( k' \), and the crystallization half-time \( t_{1/2} \) can be calculated from \( k' \) and \( n \) using eq. 7. The results are summarized in Table 8. It is evident that the corrected crystallization rate constant \( k' \) increases and \( t_{1/2} \) decreases, as the cooling rate increases, i.e., the crystallization rate is speeded up as the cooling rate increases. In general, the crystallization rate of copolymers depends on their composition. It is retarded by incorporating either ET or PT unit into the polymer backbone as a minor component.

The Avrami exponent \( n \) varies over the range of 4.67-2.43 which depends on the composition and the cooling rate. This wide range of Avrami exponents was caused by rapid cooling (or large supercooling), secondary crystallization, and relatively slower crystallization rate of copolymers. The Avrami exponent depends on the type of nucleation and the dimension of crystal growth. The trend is that \( n \) decreases with increasing cooling rate. In general, rapid cooling rate induces high crystallization rate and yields crystals with lower degree of crystallinity, therefore, secondary crystallization becomes dominate as the degree of supercooling increased. As tabulated in Table 8, the range of \( n \) values is 4.44-3.45 for C2, 3.52-2.86 for C3, 3.14-2.43 for C4, 3.95-3.32 for C6, 4.67-3.54 for C7, and 3.77-2.74 for C8.

It is useful to compare the values of the Avrami exponents, determined in this study, with those reported in the literature. Polymer TMG10 has 9.8 % trimethylene- and 90.2 % ethylene- units, and TMG60 has 60.4 % trimethylene- and 39.6 % ethylene- units. Lee et al. reported that the range of Avrami exponents for TMG10 and TMG60 are 3.31-2.83 and 2.93-2.21, respectively, for the nonisothermal
crystallization under cooling rates of 2.5-20 K/min. From the results of five copolyesters, they concluded that copolymer crystallized through three-dimension spherulitic growth with a predominant heterogeneous nucleation. For the PET/PTT copolymer with similar composition as listed in Table 1, C8, with 9.8 % trimethylene- and 90.2 % ethylene- units, has \( n \) values between 2.74 and 3.77 for cooling rates ranging from 2 to 20°C/min. C4, with 62.1 % trimethylene- and 37.9 % ethylene- units, has \( n \) values between 2.43 and 3.07 for cooling rates of 2, 5, and 10°C/min. In comparison, the values of Avrami exponents in this study are slightly higher than those done by Lee et al.\(^2\) Therefore, the values of Avrami exponents indicated that a heterogeneous nucleation and a spherulitic growth mechanism occurred during the nonisothermal crystallization of copolyesters in this study. In addition, the average values of Avrami exponents are 4.27 and 4.36, respectively, for C2 and C7 PET/PTT copolymers in the non-isothermal crystallization at a cooling rate of 1-5°C/min. Based on the reference,\(^5\) these \( n \) values correspond to 3 D spherical growth and thermal nucleation in the initial stage of crystallization where the free spherulitic growth approximation is valid.

**4.2.3 Effect of the molten temperature on the Ozawa analysis**

Let us come back to the Ozawa plot again. As discussed in section 4.2.1, the non-isothermal crystallization of C2 PET/PTT copolyester could not be described by the Ozawa equation when the molten temperature was 252°C. Changing the molten temperature from 252°C to 245 or 240°C, a series of parallel lines could be observed in Figures 7 and 8 by plotting log[\(-\ln(1-X_f)\)] versus log\(R\) over a temperature range of 20°C. For C8 copolymer, a similar situation can also be observed and is plotted in Figure 74. In general, if dynamic crystallization does not follow the Ozawa analysis, most authors attributed it to the inaccurate assumptions in the Ozawa equation. There
According to the study in our lab, both C2 and C8 PET/PTT copolyesters crystallize relatively faster than the other copolyesters do, because its composition is close to the homopolymer of PTT or PET, respectively. In general, the crystallization includes nucleation and growth. As mention above, in case the copolyester contains some nuclei, the effect of the nucleation should be able to be neglected in nonisothermal crystallization. Thus, the effect of cooling rates in the crystal growth must be considered only in non-isothermal crystallization. At the same time, induction time will be shortened, so that crystallization peak at different in cooling rates became closed. In fact, the melting condition can not be lowered unrestrictedly, because of the exothermic peak would split from one to two. Owing to the nonisothermal crystallization of C2 and C8 PET/PTT copolyester at various melting condition could follow the Ozawa equation, thus Ozawa exponent \( m \) and logarithmic cooling crystallization function \( \log F(T) \) can be obtained from the slope and intercept of the Ozawa plots and are listed in Table 4, 5 and 7, respectively. For C2 copolyester melted at 245°C, the exponent \( m \) and \( \log F(T) \) are 3.86~2.77 and 0.34~3.73 over 195~179°C, respectively. For C2 copolyester melted at 240°C, the exponent \( m \) and \( \log F(T) \) are 3.81~3.14 and -0.37~3.56 over 197~181°C, respectively. For C8 copolyester, the exponent \( m \) and \( \log F(T) \) are 2.64~2.10 and -0.12~1.58 over 202~178°C, respectively. Comparing with C3 copolyester, it found that the C2 and C8 copolyester have broader temperature range of crystallization. According to the Ozawa exponent, the nonisothermal crystallization in C2 copolymer can be concluded that it follows a heterogeneous nucleation and three-dimension spherulitic growth, regardless of melting condition. On the other hand, a heterogeneous nucleation and
three-dimension spherulitic growth occurred in the nonisothermal crystallization of C8 copolymer. In addition, it is notice that the values of Ozawa exponent \( m \) are relatively smaller than those of the Avrami exponent \( n \) which determined by using modified Avrami equation. The \( n \) values of the Avrami exponent for C2 and C8 copolyester are listed on the row first, 4th and 10th of Table 22, respectively. In general, the Ozawa exponent is usually smaller than the Avrami exponent by 0.7-0.9. The diversity between Ozawa exponent and Avrami exponent are located at a reasonable range mindedly in PET/PTT copolyester. A similar situation has been reported for the other polymers, such as Poly(ethylene isophthalate-co-terephthalate), Poly(ether ether ketone), Poly(aryl ether ether ketone ketone). There is a discrepancy between both of the analyses from these results even thought they have been derived from the same Avrami approach.

4.3 Melting Behaviors

4.3.1 Determining the mechanism of multiple endothermic peaks

In literature, multiple melting peaks are observed on heating process, and explained by three main models as described in section 2.4. For this reason, an adequate model should be selected to elucidate this phenomenon for PET/PTT copolyester system in the beginning. To start with, the X-ray diffraction pattern is good for us. For instance, WAXD patterns of C2 PET/PTT copolyester crystallized at different crystallization temperatures (i.e. 180~207°C) as shown in Figure 14 and 15. They clearly indicate that the positions of diffraction peaks do not change, except the peak height becomes sharper, while \( T_c \) increases. It reveals the crystal structure do not change within the crystallization temperature range \( i.e., \) the crystal has only one crystalline structure. As mentioned above, multiple melting behavior of C2 copolymer should not be caused by melting of the crystal which possessed different structures.
For all copolyester, similar situations are perceived as shown in Figure 28, 29, 42, 43, 55, 56, 66, 67, 81, 82 and 85. Next, according to Hoffman’s regime transition theory, the polymer crystallization can be sorted into Regime I, II, and III that relying on crystallization temperature. Crystals, formed in Regime I (closed to the equilibrium temperature), usually possess more perfect structure. When crystallization temperature is lower, crystal morphology may change from axialites to spherulites and eventually into a switchboard model, i.e. crystals become less perfect. The regime transition II → III temperatures, $T_{II→III}$ of all PET/PTT copolysters are listed in 10th column of Table 3. For example, C2 copolymer was reported to be 193.6°C. Figure 3 indicates that C2 sample mostly crystallized between Regime II and III under non-isothermal condition. In fact, all copolymers took place crystallization almost at the same regime. Moreover, regardless of composition, only single exothermic peak is observed from each DSC curve as shown in Figure 3, 19, 33, 46, 57 and 70. The similar situation has been proposed by Hobbs and Pratt and they suggested a single mode distribution in crystallite size formed during cooling process. We have convinced that the melt-crystallized sample is not composed of crystallites with a bimodal distribution. Eventually, crystals formed under non-isothermal conditions are unstable inherently, even though crystallizing at a slower cooling rate (i.e. 1°C/min) and resulting in a better (but still imperfect) crystal. Thus, melting behaviors of the PET/PTT copolymers are appropriately explained by melt-recrystallization mechanism.

4.3.2 Multiple endothermic peaks of the C2 PET/PTT copolyester

C2 copolymers were heated from room temperature to 252°C at a rate of 20°C/min and kept for 5 min to erase thermal history. Then, they crystallized non-isothermally from melts to 30°C at a constant rate (i.e.-1~20°C/min). The
melting condition is higher than the equilibrium temperature\textsuperscript{45, 46} because melting behavior is affected by its thermal history. The melt-crystallized samples were heated at a rate of 50°C/min or 2°C/min during a period of 40 sec, respectively.

At first, the melt-crystallized sample was heated at a rate of 50°C/min. In general, a rapid heating rate can suppress effectively the occurrence of the recrystallization and understand the melting temperature of original crystals which are derived from the melt under non-isothermal conditions. Figure 10 indicates that two melting peaks appeared at each heating curve, labeled as $T_{m_1}$, $T_{m_2}$, respectively with increasing degrees in temperature and their values were listed in the 8th and 9th column of Table 3. The low melting peak shifts to a higher temperature as cooling rate decreases, but the high one still remains nearly a constant (ca. 216°C) and is not sensitive to the cooling rate. In addition, the higher melting peak decreases in size at expense of the low one as cooling rate decreases. In general, the primary crystal depends on the cooling rate\textsuperscript{24} under non-isothermal condition, \textit{i.e.} polymers have enough time to form more perfect crystals at slow cooling rate. Therefore they can melt at higher temperature. According to the 6th column of Table 3, it indicates that the exothermic heat decreases a little bit as the cooling rate increases. It implies C2 PET/PTT copolyester possessing a rapid crystallization rate; hence C2 copolymer still occurs re-crystallization even at a very high heating rate. As described above, it suggested that the low-endothermic peak is attributed to the melting of primary crystals, and the higher one is the melting of the crystal generated by re-crystallization on heating. It is worthy to notice that the melting of secondary crystal was not observed clearly from DSC melting curves. Thus, we thought the secondary crystal formed uneasily under nonisothermal conditions. There is still evidence to prove the existence of secondary crystals. Upon carefully observation, we notice that there is a
tail occurring apparently at about 195-205°C close to the Peak $T_{m1}$. And it gradually disappears as cooling rate increased. Therefore, it concluded that the tail is attributed to the melting of secondary crystals. Since the 4th column of Table 3 shows the crystallization process of C2 copolymer end at 189.4°C with a cooling rate of 1°C/min. And the Figure 10 reveals the endothermic signal is detected obviously at about 195°C. It is 5.6°C difference between them. Overall, polymer isothermally crystallized at given crystallization temperature ($T_c$), and a low temperature endotherm was usually observed from about 10°C above $T_c$ at the following heating process. In literature, it was attributed to the melting of the secondary crystal. On contrast, the discrepancy under nonisothermal process is smaller than 10°C, but it is reasonable to believe. Due to the crystals formed at a nonisothermal condition and they have less complete structure than the crystallized isothermally one.

Traditional DSC measurements have some limitations, especially when multiple transitions (ex. crystallization, melting) appear in the same temperature range. For DSC total signals resulted from endothermic and exothermic process. They are often confusing and sometimes misleading, thus effective information cannot be acquired to explain melting behaviors. Temperature Modulate Differential Scanning Calorimeter (TMDSC) not only provides a total heat flow (like traditional DSC heating curves), but also reverses the non-reversing heat flow. The total heat flow curves as shown in Figure 11 are complicated. Both multiple melting peaks and exothermic events can be observed from the heating scans. There is a low-temperature melting peak (labeled as I), which occurs at total TMDSC signals. According to the study of Sauer et al., peak I is not a true “low endotherm”, but a superposition of early melting of the secondary crystal with nearly simultaneous exothermic re-crystallization. The endothermic enthalpy of the low-temperature peak, $\Delta H_{\text{endo,low}}$
value (see the column 2 of Table 10) decreases with an increasing cooling rate. The smaller the $\Delta H_{\text{endo,low}}$ is, the bigger the re-crystallization amount is. However, under cooling rate conditions of 10 and 20°C/min, exothermic peak, labeled as $I_{\text{exo}}$, emerges during the heating scan, since the amount of recrystallization are getting bigger than that of the melting. The middle peak, labeled as II, both the melting temperature and endothermic enthalpy decreased with an increasing cooling rate from the melt. On the contrary, the location of the upper melting peak, labeled as III, whose intensity increases with a decreasing cooling rate, shows no dependence on the cooling rate.

Figure 12 shows that two or three endothermic peaks appear in reversing heat flows. They are labeled as $I_R$, $II_R$, $III_R$, respectively, with increasing degrees in temperature. The melting temperature and the endothermic enthalpy of low-temperature peak $I_R$ decrease with an increasing cooling rate. The endothermic enthalpy of the middle-melting peak, $II_R$ increases as the cooling rate increases, whereas the peak temperature moves slightly to the low temperature region. In addition, peak $II_R$ decreases in size at expense of peak $I_R$ as cooling rate decreases. The high-melting peak, $III_R$ appears at about 224°C regardless of cooling rate. In Figure 13, non-reversing heat flow shows an obvious exothermic peak during heating process and its range becomes broader as the cooling rate increases. The melting enthalpy and peak temperature of TMDSC data are summarized at Tables 9 and 10.

To observe Figure 12 and 13, it is obvious that re-crystallization and melting simultaneously take place nearly by a broad temperature range. Based on the 9th and 13th columns of Table 9, in all cases, the recrystallization is detected starting promptly after melting of initial crystals at low temperature. For example, the cooling rate of 1°C/min, the crystals melt at about 186°C in a reversing signal, and then crystallization is detected from temperature ranging 199.6 to 217.2°C from
nonreversing curve. The 13th column of Table 9 revealed the higher cooling rate from the melt is, the earlier the recrystallization occurs. And the amounts of the exothermic peaks add as the cooling rate increases. As above, it clearly verifies the supposed melt-recrystallization model with observation of a distinct exothermic range in nonreversing signal and the corresponded curves in the reversing signals represent melting and remelting.

Based on the melting temperature of endothermic peaks at a heating rate of 50°C/min. It concluded that the peak $I_R$ is attributed to the melting of crystals grown by primary crystallization. The peak $II_R$ is the melting of crystals formed by recrystallization on heating. The highest melting peak $III_R$ emerged at about 224°C at reversing TMDSC signal. And it is a similar situation that could be observed from the reference.\(^{46}\) Chen has suggested that this peak is attributed to the melting of the crystal formed in Regime I during heating process. In section 4.1, we have been proposed that the regime $I \rightarrow II$ transition of C2 copolymer locate at 210~213°C. Figure 13 shows two apparent exothermic events occur on the cooling rate of 20°C/min. That implies not only the exotherm of the recrystallization, but also a thermal event (labeled as $I_{exo,NR}$) appearing at about 210~218°C before crystal melts completely. Since C2 copolymer has fast crystallization rate. Therefore it can rapidly crystallize near Regime I (although it is close to equilibrium temperature), and then melt to produce the highest endothermic peak in reversing heat flow. Thus, we suggest that peak $III_R$ is attributed to the melting of crystals formed in Regime I during heating scan as conclusion.

4.3.3 Multiple endothermic peaks of the C3 PET/PTT copolyester

C3 copolymers were heated from room temperature to 215°C at a rate of 20°C/min and kept for 5 min to erase thermal history. Then, they crystallized
non-isothermally from melts to 30°C at a constant rate \((i.e.-1\sim-20°C/min)\). The melting condition is higher than the equilibrium temperature, \(^{45,46}\) because the melting behavior is affected by its thermal history. The melt-crystallized samples were heated at a rate of 50°C/min or 3°C/min during a period of 40 sec, respectively.

At first, the melt-crystallized sample was heated at a rate of 50°C/min. In general, a rapid heating rate can suppress effectively the occurrence of the recrystallization and understand the melting temperature of original crystals which are derived from the melt under non-isothermal conditions. Figure 24 indicates that two melting peaks appear on the cooling rate of 1 and 2°C/min, but two become one as cooling rate increase. They were labeled as \(T_{m1}, T_{m2}\), respectively with increasing degrees in temperature and their values are listed in the 8th and 9th column of Table 3. The low melting peak shifts to a higher temperature as the cooling rate decreases, but the another one remains nearly constant (c.a. 184°C). In addition, peak \(I_{R}\) decreases in size at expense of peak \(I_{R}\) as cooling rate decreases. It coincides on the melt-recrystallization model, \(i.e.\) the more imperfect crystal is, the easier recrystallization occurs. In addition, on the cooling rate of 20°C/min, its melting heat is smaller than others, and taking place cold crystallization on the heating process. This is because C3 copolymer does not possess fast crystallization rate. The similar situation has been reported in C2 copolymer. The melting of secondary crystal was not observed clearly at DSC melting curves. Upon careful observation, we notice that there is a tail occurring apparently at about 145-165°C close to the Peak \(T_{m1}\) and it gradually disappearing as cooling rate increases. Therefore, it concluded that the tail is attributed to the melting of secondary crystals. For example, the 4th column of Table 3 indicated the crystallization process ended at 137.1°C with a cooling rate of 1°C/min. And the Figure 24 reveals the endothermic signal is obviously detected by
approximately 145°C. It is 7.9°C difference between them. To sum up, it is suggested that the low-endothermic peak is attributed to the melting of primary crystals, and the higher one is the melting of the crystal generated by re-crystallization during the heating process.

The total heat flow curves as shown in Figure 25 are complicate. Both endothermic and exothermic events can be observed from the heating scans. On the cooling rate at 10 and 20°C/min, cold crystallization is detected from the beginning, and their amount increases with an increasing cooling rate. As we know, the useful information can not be obtained from total heat flow, especially at slow heating rate. Figure 26 shows that three endothermic peaks appear in reversing heat flow. They are labeled as I_R, II_R, III_R, respectively, with increasing degrees in temperature. The melting temperature and the endothermic enthalpy of low-temperature peak I_R decrease with an increasing cooling rate. The endothermic enthalpy of the middle-melting peak, II_R increases as the cooling rate increases, whereas the peak temperature moves slightly to the low temperature region. In addition, peak II_R decreases in size at expense of peak I_R as cooling rate decreases. The high-melting peak, III_R appears at about 195°C. In Figure 27, non-reversing heat flow shows an obvious exothermic peak before crystals melt completely, and its range becomes broader as the cooling rate increases. In addition, there are also occur cold crystallization between 10 and 20°C/min. The melting enthalpy and peak temperature of TMDSC data are summarized at Tables 11 and 12.

To observe Figure 26 and 27, it is obvious that re-crystallization and melting simultaneously take place nearly over a broad temperature range. Based on the 10th and 14th columns of Table 11, in all cases the recrystallization is detected to start promptly after melting of initial crystals at low temperature. For example, for the
cooling rate of 1°C/min, the crystals melt at about 144°C in a reversing signal, and then crystallization is detected at temperature ranging 170.8 to 184.9°C from nonreversing curves. The 14th column of Table 11 indicates that the higher cooling rate from the melt is, the earlier the recrystallization occurs. And the amounts of the exothermic peaks add as the cooling rate increases. As above, it clearly verifies the supposed melt-recrystallization model with observation of a distinct exothermic range in nonreversing signal and the corresponded curves in the reversing signals represent melting and remelting.

Three endothermic peaks appear in reversing heat flow for cooling rate between 1 and 20°C/min. According to the melting temperature of endothermic peaks at a heating rate of 50°C/min, it concluded the low-temperature endotherm, I_R, attributed to the melting of crystals grown by primary crystallization. The middle one is the melting of crystals formed by recrystallization during the heating process. The highest melting peak IIIR emerged at about 195°C at reversing signal. The similar situation is described in the preceding section. For C3 copolymer, the regime I → II transition located at 170~174°C. Figure 27 shows an apparent broad exothermic event can be observed before crystals completely melting, especially at 20°C/min. That implies not only the exotherm of recrystallization, but also a thermal event (labeled as II’_{exo,NR}) appearing during final heating scan. As we known, C3 copolymer has slower crystallization rate then C2 copolymer. But it still crystallizes near Regime I, and then melt to produce the highest endothermic peak in reversing heat flow. As follows, we suggest that peak III_R is attributed to the melting of crystals formed in Regime I during heating scan as conclusion.

4.3.4 Multiple endothermic peaks of the C4 PET/PTT copolyester

C4 copolymers were heated from room temperature to 192°C at a rate of
20°C/min and kept for 5 min to erase thermal history. After then, they crystallized non-isothermally from melts to 30°C at a constant rate (i.e. -1~−20°C/min). Because melting behavior is affected by its thermal history, the melting condition is higher than the equilibrium temperature. The melt-crystallized samples were heated at a rate of 50°C/min or 3°C/min with a period of 40 sec, respectively.

Figure 38 shows the corresponding melting endotherms at a heating rate of 50°C/min. Only endothermic peak, with a slight shoulder on the high temperature side appeared on the lowest cooling rate (i.e. 1°C/min). Upon further increase in cooling rate, one melting peak split into two. They were labeled as Tm1, Tm2, respectively with increasing degrees in temperature and their values were listed in the 8th and 9th column of Table 3. While the cooling rate decreases, the low melting peak shifts to a higher temperature, but the high temperature melting peak still remains nearly constant (ca.170°C). However, endothermic amount decreases apparently as cooling rate increases. In fact, C4 copolymers have slower crystallization rate, since it includes higher ET mol% content. 7th column of Table 3 indicates that exothermic amount reduce rapidly as cooling rate increase. These imply that C4 copolymer crystallized or recrystallized uneasily under a rapid rate. In conclusion, it clearly indicates that the low-melting temperature peak is attributed to the melting of primary crystallization, and the high-melting temperature one is attributed to the melting of crystals formed by recrystallization during the heating process., but

Figure 39 shows that on the cooling rate at 2 and 10°C/min cold crystallization is detected in total heat flows and its amount and peak location (Icold) increase with an increasing cooling rate. Both reversing and non-reversing signals of the TMDSC are shown in Figure 40 and 41, respectively. There are three endothermic peaks in the reverse heat flow and are labeled as IR, IIIR, IIIIR, respectively, with increasing degrees
in temperature. The melting temperature and the endothermic enthalpy of low-temperature peak, $I_R$, decrease with an increasing cooling rate. The endothermic enthalpy of the middle-melting peak, $II_R$ increases as the cooling rate increases, but its peak temperature moves slightly to the low temperature region. In addition, peak $II_R$ decreases in size at expense of peak $I_R$ as cooling rate decreases. The high-melting peak, $III_R$ appears at about 182°C. Figure 41 shows two obvious exothermic events i.e. cold crystallization and recrystallization in non-reversing flow heat, except at cooling rate of 1°C/min and their exothermic amounts become much as the cooling rate increased. The melting enthalpy and peak temperature of TMDSC data are summarized at Tables 13 and 14.

Generally speaking, TMDSC provides powerful improvement to verify the melt-recrystallization phenomena. It is obvious that re-crystallization and melting simultaneously take place nearly over a broad temperature range in Figure 40 and 41. The 8th and 12th columns of Table 11 indicate that recrystallization is detected to start promptly after melting of initial crystals at low temperature. Take the cooling rate of 2°C/min for example, the crystals melt at about 105°C in a reversing signal, and then crystallization is detected at temperature ranging 125.2 to 168.8°C from nonreversing curves. The 14th column of Table 11 also indicates the higher cooling rate from the melt is, the earlier the cold crystallization occurs. As above, it clearly verifies the supposed melt-recrystallization model with observation of a distinct exothermic range in nonreversing signal and the corresponded curves in the reversing signals represent melting and remelting.

To compare with the corresponding location of melting peak between Figure 38 and 40, it can conclude the low-temperature endotherm, $I_R$, attributed to the melting of crystals grown by primary crystallization. The middle one is the melting of
crystals formed by recrystallization during the heating process. The highest melting peak III\textsubscript{R}, emerged at about 182°C at reversing signal. The similar situation has been described in C2 and C3 PET/PTT copolyesters. For C4 copolymer, the regime I \rightarrow II transition located at 164–168°C. An apparent broad exothermic event, labeled as II'\textsubscript{exo,NR} (i.e. 150–168°C) can be observed in Figure 41, except at cooling rate of 1°C/min. Thus, we suggest that peak III\textsubscript{R} is attributed to the melting of crystals formed in Regime I during heating scan as conclusion. Although crystallization rate of C4 copolymer is slower than C3 copolymer, it still crystallizes near Regime I, and then melt to produce the highest endothermic peak in reversing heat flow.

4.3.5 Multiple endothermic peaks of the C6 PET/PTT copolyester

C6 copolymers were heated from room temperature to 228°C at a rate of 20°C/min and kept for 5 min to erase thermal history. After then, they crystallized non-isothermally from melting to 30°C at a constant rate (i.e.-1~20°C/min). Because melting behavior is affected by its thermal history, the melting condition is higher than the equilibrium temperature.\textsuperscript{45,46} The melt-crystallized samples were heated at a rate of 50°C/min or 3°C/min with a period of 40 sec, respectively.

Figure 51 shows the corresponding melting endotherms at a heating rate of 50°C/min. Two endothermic peaks emerged at each heating curve, labeled as T\textsubscript{m1}, T\textsubscript{m2}, respectively, with increasing degrees in temperature and their values were listed in the 8th and 9th column of Table 3. Both the low-melting and high-melting peaks gradually shift to a higher temperature region as the cooling rate decreases, and their endothermic amounts also increase at the same time. For C6 copolymer, the 5th column of Table 3 indicates that crystallization process ends at 149.4°C with a cooling rate of 1°C/min. And the Figure 50 shows the endothermic signal is obviously detected at about 160°C. It is about 10°C different between them. The similar
situation has been reported in previous section, and it is reasonable to believe that the low-melting peak is caused by the melting of secondary crystals. In general, the primary crystal depends on the cooling rate\textsuperscript{24} under non-isothermal condition, \textit{i.e.} polymers have enough time to form more perfect crystals at slow cooling rate, and therefore they can melt at higher temperature. It concludes high-melting peak attributed to the melting of crystal form at primary crystallization.

Two to three endothermic peaks emerge in total heat flows of TMDSC, as shown in Figure 52. They are labeled as I, II, III, respectively, with increasing degrees in temperature. Both the melting temperature and the endothermic enthalpy of the peak I and II decrease with an increasing cooling rate from the melt. The peak III (or shoulder) appears almost at the same location (~205°C), but it increases in size at expense of the middle melting peak as cooling rate increases. On the cooling rate at 10°C/min, cold crystallization is detected in the beginning during heating scan. To compare with corresponding location of melting peak between Figure 51 and 52, it was found the first two peaks that had a little difference in melting temperature i.e., $T_{m1} > I$, $T_{m2} < II$. Because of they were heated at various rates. In Figure 53, a broader endothermic range appeared, but it can be divided into three parts in detail including tail, peak and shoulder. And they are labeled as $I_R$, $II_R$, $III_R$, respectively with increasing degrees in temperature. When cooling rate decreased the middle-melting peak gradually shifted to a higher temperature region and the high-melting peak (or shoulder) keeps almost at the same location, but it increases in size at expense of the middle melting peak. The non-reversing signal of TMDSC shown in Figure 54, it shows polymer take place recrystallization in heating process, and exothermic amount and range increases as cooling rate increases. All melting temperatures and thermal events were obtained from the TMDSC signals and
summarized in Table 15 and 16. In fact, another higher endothermic event, a shoulder, emerged in total and reversing signals of TMDSC. The melt-recrystallization model indicated that when crystal was heated at a slow rate, thus it had enough time to take place recrystallization during heating process. Therefore recrystallization phenomena is not observed at rapid heating rate i.e. 50°C/min. As described above, both III and III_R arose from the melting of crystal formed during recrystallization process. Non-reversing curves are able to verify the existence of recrystallization. For example, on the cooling rate of 10°C/min, a broad exothermic event (I_{exo, NR}) is detected at temperature ranging 135.4 to 195.9°C, and the ∆H_{exo, NR} value increases as cooling rate increases. In addition, ∆H_{endo, total} values obtained from the 6th column of Table 16, are bigger than ∆H_c. As mentioned above, the peak I and I_R are attributed to the melting of crystals grown by secondary crystallization and the peak II and II_R are the melting of crystals formed by primary crystallization and the peak III and III_R are attributed to the melting of crystal by melt-recrystallization.

4.3.6 Multiple endothermic peaks of the C7 PET/PTT copolyester

C7 copolymers were heated from room temperature to 234°C at a rate of 20°C/min and kept for 5 min to erase thermal history. Then, they crystallized non-isothermally from melts to 30°C at a constant rate (i.e.-1~20°C/min). The melting condition is higher than the equilibrium temperature \(^{45, 46}\) because melting behavior is affected by its thermal history. The melt-crystallized samples were heated at a rate of 50°C/min or 3°C/min with a period of 40 sec, respectively.

Figure 62 shows the corresponding melting endotherms at a heating rate of 50°C/min. Two endothermic peaks emerged at each heating curve, labeled as T_m1, T_m2, respectively, with increasing degrees in temperature and their values were listed in the 8th and 9th column of Table 3. Both the low-melting and high-melting peaks
gradually shift to a higher temperature region as the cooling rate decreases, and their endothermic amounts also increase at the same time. For C7 copolymer, the 5th column of Table 3 indicates that crystallization process ends at 145.6°C with a cooling rate of 1°C/min. And the Figure 62 shows the endothermic signal is detected obviously at about 160°C. It is about 15°C difference between them. The similar situation has been reported in previous section, and thus it is reasonable to believe that the low-melting peak is caused by the melting of secondary crystals. In general, the primary crystal depends on the cooling rate under non-isothermal condition, *i.e.*, Polymers have enough time to form more perfect crystals at slow cooling rate, and therefore they can melt at higher temperature. It concludes high-melting peak attributed to the melting of crystal form at primary crystallization.

Two to three endothermic peaks emerge in total heat flows of TMDSC, as shown in Figure 63. They are labeled as I, II, III, respectively, with increasing degrees in temperature. Both the melting temperature and the endothermic enthalpy of the peak I and II decrease with an increasing cooling rate from the melt. The peak III (or shoulder) appears almost at the same location (~215°C), but it increases in size at expense of the middle melting peak as cooling rate increases. To compare corresponding location of melting peak between Figure 62 and 63, it was found the first two peaks that had a little difference in melting temperature *i.e.*, $T_{m1} > I$, $T_{m2} < II$. Because of they were heated at various rates. In Figure 64, a broader endothermic range appeared, but it can be divided into three parts in detail including tail, peak and shoulder. And they are labeled as $I_R$, $II_R$, $III_R$, respectively with increasing degrees in temperature. When cooling rate decreased the middle-melting peak gradually shifted to a higher temperature region and the high-melting peak (or shoulder) keeps almost at the same location, but it increases in size at expense of the middle melting peak.
The non-reversing signal of TMDSC shown in Figure 65 it shows polymer take place recrystallization in heating process, and exothermic amount and range increases as cooling rate increases. All melting temperatures and thermal events were obtained from the TMDSC signals and summarized in Table 17 and 18. In fact, another higher endothermic event, a shoulder, emerged in total and reversing signals of TMDSC. The melt-recrystallization model indicated that when crystal was heated at a slow rate, thus it had enough time to take place recrystallization during heating process. Therefore recrystallization phenomena is not observed at rapid heating rate i.e. 50°C/min. As described above, both III and III_R arose from the melting of crystal formed during recrystallization process. Non-reversing curves are able to verify the existence of recrystallization. For example, on the cooling rate of 20°C/min, a broad exothermic event (I_{exo,NR}) is detected at temperature ranging 135.3 to 205.3°C, and the $\Delta H_{exo,NR}$ value increases as cooling rate increases. In addition, $\Delta H_{endo,total}$ values obtained from the 6th column of Table 18, are bigger than $\Delta H_c$. As mentioned above, the peak I and I_R is attributed to the melting of crystals grown by secondary crystallization and the peak II and II_R is the melting of crystals formed by primary crystallization and the peak III and III_R is attributed to the melting of crystal by melt-recrystallization.

**4.3.7 Multiple endothermic peaks of the C8 PET/PTT copolyester**

C8 copolymers were heated from room temperature to 276°C at a rate of 20°C/min and kept for 5 min to erase thermal history. Then, they crystallized non-isothermally from melts to 30°C at a constant rate (i.e.-1~20°C/min). The melting condition is higher than the equilibrium temperature because melting behavior is affected by its thermal history. The melt-crystallized samples were heated at a rate of 50°C/min or 3°C/min with a period of 40 sec, respectively.
Figure 77 shows the corresponding endotherms at a heating rate of 50°C/min. Two peaks emerged and merged gradually, then become one as cooling rate increase. They are labeled as $T_{m1}$ and $T_{m2}$ respectively, with increasing degrees in temperature and listed in the 8th and 9th column of Table 3. The lower melting temperature peak shifts to a high temperature region as cooling rate increases, but it seems to be that arrested to higher one by peak $T_{m2}$ on the cooling rate of 5 and 20°C/min. It is due to C8 copolymer possess fast crystallization rate, and thus it can crystallized at rapid heating rate. The high melting temperature peak remains at about 236°C, and endothermic amount decreases in size at expense of the lower one. In conclusion, it concluded that the peak $T_{m1}$ is attributed to crystal form at primary crystallization and the peak $T_{m2}$ is attributed to the melting of crystal formed by recrystallization. In addition, there is a tail exist at lower temperature side of Peak $T_{m1}$, and its amount decreased gradually as cooling rate increased. Similar situation has been reported in previous sections, and thus it can be attributed to the melting of crystals formed during secondary crystallization.

Figure 78 indicated that a broader endothermic peak emerges during heating scan. It can be divided into three parts in detail, and labeled as I, II, III, respectively, with increasing degrees in temperature. In fact, useful information can not be obtained from total heat flows of TMDSC as previous conclusion. In Figure 79, a broader endothermic range appeared, but it can be divided into three parts in detail including tail, peak and shoulder. And they are labeled as $I_R$, $II_R$, $III_R$, respectively with increasing degrees in temperature. When cooling rate decreased the middle-melting peak gradually shifted to a higher temperature region and the high-melting peak (or shoulder) keeps almost at the same location, but it increases in size at expense of the middle melting peak. The non-reversing signal of TMDSC as shown in Figure 80, it
shows polymer take place recrystallization in heating process, and exothermic amount and range increases as cooling rate increases. All melting temperatures and thermal events were obtained from the TMDSC signals and summarized in Table 19 and 20. Reversing and non-reversing curves are able to verify the existence of melt-recrystallization. For example, on the cooling rate of 1°C/min, the crystals melt partly at about 162°C in a reversing signal. And then recrystallization is detected at temperature ranging 193.3 to 235.5°C, then re-melts from non-reversing curves. As mentioned above, the peak I and I_R is attributed to the melting of crystals grown by secondary crystallization and the peak II and II_R is the melting of crystals formed by primary crystallization and the peak III and III_R is attributed to the melting of crystal by melt-recrystallization. It is worthy to notice, Table 3 indicated that regime I → II transition of C8 copolymer locates at 228~232°C. However the higher melting peak which like to C2-C4 copolymer, can not be observed from reversing heat flow. Maybe C8 copolymer had high ET mole% content i.e. 91~93%.

4.3.8 Summary

Multiple melting behaviors have been able to be appropriately explained by melt-recrystallization mechanism. Therefore, we classify those copolymers into three types according to their melting behaviors. C2-C4 copolyesters (high PT mol% content) exhibited two special properties as followed the melting of secondary crystal is not easily observed from heating process. The highest melting peak emerges in reversing heat flow and is attributed to crystal formed in Regime I. C6 and C7 copolyester revealed apparent distinction between the melting of secondary and primary crystal. C8 copolymer shows the melting of secondary crystal is not easily observed from heating process likely C2-C4 copolymer, but the highest melting peak does not emerges in reversing heat flow.
4.4 Cocrystallization behavior of PET/PTT copolyesters

The cocrystallization behavior of copolymer is usually confirmed by carrying out DSC and WAXD measurement. At first, Figure 83 shows the heating and cooling thermograms of the melt-quenched samples (those quenched into liquid nitrogen). For all PET/PTT copolyester, a clear endothermic and an exothermic peak are observed, which may be a strong evidence for cocrystallization. Furthermore, the change of melting and crystallization temperatures with the ET composition revealed a typical eutectic behavior, indicating that the PET/PTT copolyesters exhibited an isodimorphic cocrystallization. The minimum melting temperature is observed at the composition of 50 mol% ET. As can be seen in cooling thermograms of Figure 83(B), the $T_c$ becomes lower and broader as the comonomer content increase. It means that the crystallization rates of the copolymers decrease with increase the corresponding comonomer content, due to an addition restriction of comonomer on the formation of each crystal lattice. It has been known that the comonomer concentration in cocrystal lattice is dependent on the copolymer composition and the crystallization condition.

The extent of cocrystallization can qualitatively determined by the change of the lattice $d$ spacing in the WAXD pattern. The previous results have indicated that WAXD patterns can not change as the crystallization temperature increase, regardless of composition. As a result, Figure 84 displayed the WAXD patterns which copolymer crystallized at the given the highest $T_c$. All copolyesters possessed sharp diffraction peaks through the entire range of copolymer composition, and WAXD patterns can be sorted two groups according to the ET content in the copolymer. The PTT type crystal structure develops up to 38 mol % ET content *i.e.* The PTT lattice accommodates the ET units, although above 72 mol % ET, the PET type crystal structure dominates. Those WAXD patterns also supported the isodimorphic cocrystallization of PET/PTT.
copolyester. Another point is to be noted that the diffraction pattern of PT50/ET50 copolyester differed greatly from those of other copolyester. It confidently hypothesize that the crystalline phase changes from PET or PTT type crystal to a new crystal structure in the composition of 50 % mol ET content. As a consequence of comonomer inclusion, the $d$ spacings of both crystal structures change with the comonomer content. As shown in Figure 85, in the PTT type both the $d(100)$ and the $d(010)$ spacing slightly decreases with increasing ET content. However, in the case of PET type crystal, both the $d(100)$ and the $d(010)$ spacings are almost constant irrespective of the PT content.

Figure 89 and 90 showed X-ray diffraction patterns of well-oriented PET/PTT copolyesters fibers, and symmetrical arcs can be clearly seen. It also found that most copolyesters produced fiber diffraction patterns with similar spacings and intensities to those of PET\textsuperscript{59} and PTT.\textsuperscript{51} Therefore indexing of those patterns of copolymers (except C4 and C5 copolymer) could be made on the basis of the triclinic crystal lattice of PET with parameters $a_0 = 4.56$ Å, $b_0 = 5.94$ Å, $c_0 = 10.75$ Å, ($\alpha = 98.5^\circ$, $\beta = 98.5^\circ$, and $\gamma = 98.5^\circ$), or that of PTT with parameters $a_0 = 4.63(7)$ Å, $b_0 = 6.26(6)$ Å, $c_0 = 18.64$ Å, ($\alpha = 98.4^\circ$, $\beta = 93.0^\circ$, and $\gamma = 111.1^\circ$). The results of WAXD patterns and fiber diagrams were listed in Table 24. It indicated that the extremely good coincident of these spacings with those of PET and PTT in fiber patterns. As mentioned above, it concluded that the crystallized PET/PTT copolymers adopt the same triclinic crystal structures as PET and PTT. Similar situation also was found in powder diffraction pattern. Since the ET or PT unit should be excluded from the crystal structure of PET and PTT, respectively. It is worth to pay attention. Figure 84 has shown that a new phase produced in the copolyester with 50 mol\% ET content, but fiber patterns indicated that a new crystalline phase is observed in the copolyester.
with 37 mol% ET. In conclusion, C5 copolyester indeed possesses a new crystalline structure and it is similar to PTT crystal structure. Therefore it also belongs to triclinic system. If we would want to know the true crystal structure of C5 copolyester, the diffraction peaks or planes should be furthermore indexed in WAXD and fiber patterns. However, it is difficult for us at the moment, because a few diffraction peaks or planes can be acquired only.

4.5 Crystal structure of C5 PET/PTT copolyester

Figure 86 indicated that WAXD patterns exhibited that several diffraction peaks are clearly observed and remain unchanged irrespective of crystallization temperatures. Since it is concluded that the crystal transformation induced by temperature does not appear in C5 copolymer. The same situation also was observed in IR spectra shown in Figure 87. Figure 88 shows the infrared spectra for amorphous and crystalline C5 copolymer in the 600-1800 cm\(^{-1}\) region. In literature,\(^6^3\) Ward and Wilding had been reported and assigned the IR and Raman spectra of poly(m-methylene terephthalate), including PET, PTT and PBT. To Compare the IR spectra of PET and PTT with our C5 copolyester, we found that band only slightly shifted. For this reason, the Table 2 of reference 63 can be applied at C5 copolymer. As mentioned above, it implied that there is no other conformations exist in C5 copolymer. In literature,\(^6^6,^6^7\) the pair peaks at 1473 and 1455 cm\(^{-1}\) (CH\(_2\) deformation, trans and gauche) were used to determined crystallinity in PET. As we known, the structure of the crystalline regions of PET shows only trans glycol conformations. In addition, PTT shows an infra-red band at 1045 cm\(^{-1}\) which is considered to be analogues to the band 1042 cm\(^{-1}\) in PET, which assigned to an Ag C-C stretching mode of a gauche conformation This band in PTT intensifies on annealing, consistent with structure knowledge of PTT, which suggest an all gauche sequence in the
crystalline region. For C5 copolymer, both intensities of the 1473 and 1410 cm\(^{-1}\) band have increased clearly after annealed. In conclusion, C5 copolymer possessed the same conformation as PET and PTT in crystalline region.

Most important in X-ray fiber diagram is the distance between the first layer and the equatorial line which corresponding to a crystallographic repeat length. The fiber diagram shown in Figure 89(d), and it had four strong arcs and two weak ones. Note that deviations in the d-spacing values of fiber diagram with respect to the powder patterns are less then 5%. The observed fiber repeat is about 9 Å, but it is short. The randomness parameter listed in Table 1 indicated that C5 copolymer is belonged to random copolyester. However, the ET and PT content are rather close (i.e. 1:1). Therefore, it has chance to form alternating copolyester under polycondensation. However, the distance between layers one and two is about 10 Å. Thus, we assumed the first layer can not be observed. Since the real fiber repeat unit may is about 20 Å for C5 copolyester. As known, the crystallographic repeat lengths of PET and PTT are 10.7 and 9.15 Å, respectively. In conclusion, the C5 repeat unit may is composed of one PET and one PTT molecule. However, those assumptions still need to be verified by other experience.
5. Conclusion

Non-isothermal crystallization and melting behavior of PET/PTT copolyesters were carried out by TA Q100. Regardless of composition, the heat of crystallization ($\Delta H_c$), the onset crystallization temperature ($T_{on}$) and crystallization peak temperature ($T_p$) decrease as cooling rate increases. The dynamic crystallization kinetics was analyzed by using Ozawa equation and the modified Avrami equation. For most copolyesters, their nonisothermal crystallization kinetics could not be described by Ozawa equation, except for C3 PET/PTT copolymer, and its Ozawa exponents, $m$ ranging from 2.68 to 3.24 at temperature range 141~150°C. As a result, it suggested that a predetermined nucleation and three-dimension growth of the crystallites. In fact, crystallization behavior of copolymer do not follow Ozawa equation, due to some factors neglected in the Ozawa analysis, such as the effect of secondary crystallization, dependence of lamellar thickness on crystallization temperature and variation of Avrami exponent with crystallization temperature. However, non-isothermal crystallization kinetics was analyzed fitly by modified Avrami equation. Both the $n$ values and $t_{1/2}$ decreases, as the cooling rate increase while the $k'$ increase. According to the Avrami exponent of these copolyesters are respectively C2 (4.44-3.45), C3 (3.52-2.86), C4 (3.14-2.43), C6 (3.95-3.32), C7 (4.67-3.54), C8 (3.77-2.74). They indicated that followed a heterogeneuos nucleation and spherulitic growth mechanism in the primary crystallization. The average values of $n$ are 4.27 and 4.36 for C2 and C7 PET/PTT copolymer, respectively in non-isothermal crystallization at cooling rate (1~5°C/min), which corresponding to 3D spherical growth and thermal nucleation in the initial stage of crystallization where the free spherulitic growth approximation is valid. It worthy to notice, when C2 copolymer lowed down melting condition from 252°C to 245°C or 240°C, respectively and C8 copolymer lowed down melting condition from 276°C to 270°C.
We found that a series of parallel lines could be obtained from Ozawa plot. This may be due to the effect of nucleation can be neglected under crystallization.

The melt-crystallized copolymers which prepared at different cooling rates were heated at a rate of 50°C/min or 2(or 3)°C/min with a period of 40 seconds, respectively, and they exhibited two or three melting peaks on heating. Regardless of composition, WAXD patterns of those copolyesters which crystallized at various T_c's shown that their positions did not change apparently, but their peaks became stronger as T_c increased. This implies that the melting behaviors were not caused by the melting of crystals which possess different crystal structures. In addition, there is one exothermic peak appears, regardless of the cooling rates and compositions. It indicated that a single–mode distribution in crystallite size is formed during cooling process. Basically, polymer crystallized non-isothermally from the melt, inherently possess less perfect crystals, thus it easily took place crystallization on heating. As mentioned above, multiple melting behaviors have been explained by melt-recrystallization model. Therefore, when three endothermic peaks appear on heating, the low-melting temperature peak (usually a tail) is attributed to the melting of less perfect crystals formed at secondary crystallization, the middle melting peak is attributed to the melting of crystals formed in primary crystallization under non-isothermal condition, and the highest melting peak is attributed to the melt-recrystallization remelting. In the cases of the C2-C4 copolyester, three endothermic peaks occur in the reversing signals of TMDSC. It is believed the highest melting peak is attributed to melting of crystals which formed in regime I during TMDSC scan at a rate of 2 or 3°C/min.

Nevertheless, for all copolymer composition, there is exists a clear endothermic and an exothermic peak, which is a strong evidence for cocrystallization. The eutectic
melting temperature could be observed for copolyester with 50 %mol ET content. As a result of, the PET/PTT copolyesters showed a strong isodimorphic cocrystallization behavior. In addition, those WAXD patterns were able to be sorted two groups according to the ET content in the copolymer i.e. PET type and PTT type crystals. They also support the isodimorphic cocrystallization of PET/PTT copolyester. From the WAXD patterns, it indicates that crystalline transition appeared between 37.9 and 72.5 mol% ET, and C5 copolyester possessed a new crystalline phase. The IR spectra indicate that the glycol conformations of new crystalline structure are the same as that of PET and PTT in the crystalline region. In the end, according to fiber diagrams, it may hypothesize that the repeat unit of C5 PET/PTT is composed of one PET and one PTT molecules.
References


[14] Avrami, M., Kinetics of Phase Change III. Granulation, Phase Change and


[52] Ho, R.-M., Ke, K.-Z., Chen, M., Crystallization and Banded Spherulite of Poly(trimethylene terephthalate), Macromolecules, 2000, 33, 7529-75.


Table 1. The compositions, the randomness parameter (\(B\)) and the average-number sequence lengths of PT and ET units.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PT(%)</th>
<th>ET(%)</th>
<th>(B)</th>
<th>(^a)Ln(_{PT})</th>
<th>(^b)Ln(_{ET})</th>
<th>PT(%)</th>
<th>ET(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From (^{13})C-NMR</td>
<td>From (^{1})H-NMR</td>
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<td></td>
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<td></td>
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<td>10.24</td>
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<td>2.65</td>
<td>1.62</td>
<td>62.34</td>
<td>37.66</td>
</tr>
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<td>C5</td>
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<td>50.11</td>
<td>0.98</td>
<td>2.03</td>
<td>2.04</td>
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\(^a\), \(^b\); the average-number sequence lengths of PT and ET units.

From Reference [45].

Table 2. Equilibrium melting temperature and melting condition of the PET/PTT copolyester.

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<tr>
<th>Sample code</th>
<th>(^a)(T_m)</th>
<th>(^b)(T_m) ((\square))</th>
<th>(^c)(T_m) ((\square) (R))</th>
<th>(^d)(T_m)</th>
<th>(^e)(T_m)</th>
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<td>C8</td>
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<td>--</td>
<td>270</td>
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</table>

\(^a\); Evaluated by Hoffman-WeeK plots[45].
\(^b\); Evaluated by Hoffman-WeeK from total heat flow of TMDSC measurement [46].
\(^c\); Evaluated by Hoffman-WeeK from reversing heat flow of TMDSC measurement[46].
\(^d\); Melting condition of Wide-angle X-ray diffraction measurement.
\(^e\); Melting condition of Nonisothermal Crystallization.
Table 3. Nonisothermal Crystallization and Melting Data of Poly[(ethylene)-co-(trimethylene terephthalate)]s

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Cooling rate</th>
<th>$T_{on}$</th>
<th>$T_P$</th>
<th>$T_{end}$</th>
<th>$\Delta T_1$</th>
<th>$\Delta H_c$</th>
<th>$T_{m1}^b$</th>
<th>$T_{m2}^b$</th>
<th>$T_{II\to III}^c$</th>
<th>$T_{I\to II}^d$</th>
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<td>48.27</td>
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<td>216.5</td>
<td>193.6</td>
<td>210~213</td>
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<td>10</td>
<td>191.2</td>
<td>179.5</td>
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<td>shoulder</td>
<td>147.3</td>
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<td>170.4</td>
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</table>

$T_{on}$, $T_P$, $T_{end}$: The start, maximum, finish of temperature during non-isothermal crystallization.

$\Delta T_1 = T_{on} - T_P$

$^b$ Heating rate: 50°C/min

$^c$ $T_{II\to III}$: Obtained from reference [45].

$^d$ $T_{I\to II}$: Obtained from the thermograms of the melt-crystallized copolyesters at a heating rate of 80°C/min.
(Continued)

<table>
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<th>Copolymer</th>
<th>Cooling rate</th>
<th>$T_{on}$</th>
<th>$T_P$</th>
<th>$T_{end}$</th>
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<th>$\Delta H_c$</th>
<th>$T_{m1}$</th>
<th>$T_{m2}$</th>
<th>$T_{II\leftrightarrowIII}$</th>
<th>$T_{I\leftrightarrowII}$</th>
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<td>shoulder</td>
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</tbody>
</table>

$T_{on}$, $T_P$, $T_{end}$: The start, maximum, finish of temperature during non-isothermal crystallization.

$\Delta T_1 = T_{on} - T_P$

$^b$ Heating rate: 50°C/min

$^c$ $T_{II\leftrightarrowIII}$: Obtained from reference [45].

$^d$ $T_{I\leftrightarrowII}$: Obtained from the thermograms of the melt-crystallized copolyesters at a heating rate of 80°C/min.
### Table 4. Ozawa exponent m and Cooling function $F(T)$ of C2 copolyester at different temperatures. (Melting condition: 245°C, hold 5 min)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ozawa exponent, $m$</th>
<th>log$F(T)$</th>
</tr>
</thead>
<tbody>
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<td>195</td>
<td>3.69</td>
<td>0.34</td>
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<tr>
<td>191</td>
<td>3.86</td>
<td>1.44</td>
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<td>187</td>
<td>3.39</td>
<td>2.16</td>
</tr>
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<td>183</td>
<td>3.42</td>
<td>2.93</td>
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<tr>
<td>179</td>
<td>3.73</td>
<td>3.73</td>
</tr>
<tr>
<td>175</td>
<td>2.77</td>
<td>3.41</td>
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</table>

### Table 5. Ozawa exponent m and Cooling function $F(T)$ of C2 copolyester at different temperatures. (Melting condition: 240°C, hold 5 min)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ozawa exponent, $m$</th>
<th>log$F(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>197</td>
<td>3.77</td>
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</tr>
<tr>
<td>193</td>
<td>3.14</td>
<td>0.60</td>
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<tr>
<td>189</td>
<td>3.31</td>
<td>1.59</td>
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<td>184</td>
<td>3.81</td>
<td>3.08</td>
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<td>181</td>
<td>3.67</td>
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<tr>
<td>177</td>
<td>3.12</td>
<td>3.55</td>
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</table>

### Table 6. Ozawa exponent m and Cooling function $F(T)$ of C3 copolyester at different temperatures. (Melting condition: 215°C, hold 5 min)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ozawa exponent, $m$</th>
<th>log$F(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
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<td>149</td>
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<td>3.08</td>
<td>2.02</td>
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<tr>
<td>141</td>
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### Table 7. Ozawa exponent m and Cooling function $F(T)$ of C8 copolyester at different temperatures. (Melting condition: 270°C, hold 5 min)

<table>
<thead>
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<th>Temperature (°C)</th>
<th>Ozawa exponent, $m$</th>
<th>log$F(T)$</th>
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</thead>
<tbody>
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<tr>
<td>196</td>
<td>2.38</td>
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<td>190</td>
<td>2.36</td>
<td>0.87</td>
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<tr>
<td>183</td>
<td>2.49</td>
<td>1.58</td>
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<tr>
<td>178</td>
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<td>1.57</td>
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<td>Copolyester</td>
<td>Avrami Parameter</td>
<td>Cooling rate (°C/min)</td>
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<tr>
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<td>( k' )</td>
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<tr>
<td></td>
<td>( t_{1/2} )</td>
<td>358.7</td>
</tr>
<tr>
<td>C3</td>
<td>( n )</td>
<td>3.46</td>
</tr>
<tr>
<td></td>
<td>( k' )</td>
<td>2.95 \times 10^{-11}</td>
</tr>
<tr>
<td></td>
<td>( t_{1/2} )</td>
<td>1032.1</td>
</tr>
<tr>
<td>C4</td>
<td>( n )</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>( k' )</td>
<td>3.57 \times 10^{10}</td>
</tr>
<tr>
<td></td>
<td>( t_{1/2} )</td>
<td>907.8</td>
</tr>
<tr>
<td>C6</td>
<td>( n )</td>
<td>3.93</td>
</tr>
<tr>
<td></td>
<td>( k' )</td>
<td>1.20 \times 10^{-11}</td>
</tr>
<tr>
<td></td>
<td>( t_{1/2} )</td>
<td>547.4</td>
</tr>
<tr>
<td>C7</td>
<td>( n )</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>( k' )</td>
<td>6.37 \times 10^{-13}</td>
</tr>
<tr>
<td></td>
<td>( t_{1/2} )</td>
<td>795.1</td>
</tr>
<tr>
<td>C8</td>
<td>( n )</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>( k' )</td>
<td>3.15 \times 10^{-10}</td>
</tr>
<tr>
<td></td>
<td>( t_{1/2} )</td>
<td>752.5</td>
</tr>
</tbody>
</table>

\( n \): the Avrami exponent
\( k' \): the corrected rate constant of crystallization
\( t_{1/2} \) (sec.): the crystallization half-time
**Table 9.** TMDSC data of C2 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 2 °C /min with a period of 40 s (all temperature in °C)

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>Total heat flow</th>
<th>Reversing heat flow</th>
<th>Nonreversing heat flow</th>
<th>Crystallization Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>□</td>
<td>□_exo</td>
<td>□ R</td>
<td>□_exo, NR</td>
</tr>
<tr>
<td>1</td>
<td>211.6</td>
<td>--</td>
<td>221.9</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>209.4</td>
<td>212.2</td>
<td>220.5</td>
<td>209.9</td>
</tr>
<tr>
<td>5</td>
<td>206.1</td>
<td>208.6</td>
<td>218.7</td>
<td>222.7</td>
</tr>
<tr>
<td>10</td>
<td>--</td>
<td>203.9</td>
<td>217.4</td>
<td>222.8</td>
</tr>
<tr>
<td>20</td>
<td>--</td>
<td>200.5</td>
<td>shoulder</td>
<td>222.8</td>
</tr>
</tbody>
</table>

-- : not detected

**Table 10.** TMDSC (2 °C/min) data for C2 copolyester after crystallized nonisothermally from the molten state at different cooling rate including heats of melting and crystallization (all temperature in °C)

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>□_endo,low*</th>
<th>□_endo, NR</th>
<th>□_endo, NR</th>
<th>□_endo</th>
<th>□_endo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J/g</td>
<td>J/g</td>
<td>J/g</td>
<td>J/g</td>
<td>J/g</td>
</tr>
<tr>
<td>1</td>
<td>--</td>
<td>14.02</td>
<td>25.10</td>
<td>40.95</td>
<td>52.54</td>
</tr>
<tr>
<td>2</td>
<td>7.28</td>
<td>18.41</td>
<td>24.83</td>
<td>42.89</td>
<td>49.93</td>
</tr>
<tr>
<td>5</td>
<td>5.58</td>
<td>21.56</td>
<td>22.17</td>
<td>46.79</td>
<td>47.56</td>
</tr>
<tr>
<td>10</td>
<td>2.44</td>
<td>27.12</td>
<td>20.41</td>
<td>52.13</td>
<td>46.36</td>
</tr>
<tr>
<td>20</td>
<td>1.34</td>
<td>28.82</td>
<td>19.93</td>
<td>55.94</td>
<td>45.76</td>
</tr>
</tbody>
</table>

*Obtained from the total heat flow
Table 11. TMDSC data of C3 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3°C/min with a period of 40 s. All temperature in °C.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>( \Delta H_{\text{cold}} )</th>
<th>( \Delta H_{\text{exo}} )</th>
<th>Reversing heat flow</th>
<th>Nonreversing heat flow</th>
<th>Crystallization Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>99.1</td>
<td>161.9</td>
<td>99.1</td>
<td>165.8</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>159.8</td>
<td>192.6</td>
<td>159.8</td>
<td>192.6</td>
<td>159.8</td>
</tr>
<tr>
<td></td>
<td>122.0~183.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

-- : not detected

Table 12. TMDSC data for C3 copolyester after crystallized nonisothermally from the molten state at different cooling rate including heats of melting and crystallization.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>( H_{\text{endo, NR}} ) low</th>
<th>( H_{\text{cold, NR}} )</th>
<th>( H_{\text{exo, NR}} )</th>
<th>( H_{\text{endo, NR}} )</th>
<th>( H_{\text{endo, R}} )</th>
<th>( H_{\text{cold-endo}} )</th>
<th>( H_{\text{exo}} )</th>
<th>( H_{\text{endo}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6.39</td>
<td>--</td>
<td>-4.30</td>
<td>17.35</td>
<td>25.70</td>
<td>--</td>
<td>--</td>
<td>42.25</td>
</tr>
<tr>
<td>2</td>
<td>2.89</td>
<td>--</td>
<td>-8.41</td>
<td>16.23</td>
<td>27.88</td>
<td>--</td>
<td>--</td>
<td>36.88</td>
</tr>
<tr>
<td>5</td>
<td>--</td>
<td>--</td>
<td>-12.25</td>
<td>14.30</td>
<td>34.17</td>
<td>--</td>
<td>--</td>
<td>35.51</td>
</tr>
<tr>
<td>10</td>
<td>--</td>
<td>-8.63</td>
<td>-14.74</td>
<td>13.84</td>
<td>35.98</td>
<td>-8.59</td>
<td>-1.25</td>
<td>31.61</td>
</tr>
<tr>
<td>20</td>
<td>--</td>
<td>-17.38</td>
<td>-14.42</td>
<td>14.11</td>
<td>35.82</td>
<td>-17.85</td>
<td>-1.56</td>
<td>29.87</td>
</tr>
</tbody>
</table>

-- : not detected

\* Obtained from the Nonreversing heat flow
Table 13. TMDSC data of C4 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3 °C/min with a period of 40 s. All temperature in °C.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>Total heat flow</th>
<th>Reversing heat flow</th>
<th>Nonreversing heat flow</th>
<th>Crystallization Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta_h$</td>
<td>$\Delta_h$</td>
<td>$\Delta_h$</td>
<td>$\Delta_h$</td>
</tr>
<tr>
<td>1</td>
<td>169.6</td>
<td>179.6</td>
<td>169.5</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>110.8</td>
<td>--</td>
<td>178.1</td>
<td>159.3</td>
</tr>
</tbody>
</table>

-- : not detected

Table 14. TMDSC data of C4 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3 °C/min with a period of 40 s, including heats of melting and crystallization.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>$\Delta_h^{\text{exo, NR}}$</th>
<th>$\Delta_h^{\text{exo, R}}$</th>
<th>$\Delta_h^{\text{endo, NR}}$</th>
<th>$\Delta_h^{\text{endo, R}}$</th>
<th>$\Delta_h^{\text{exo}}$</th>
<th>$\Delta_h^{\text{endo}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>23.98</td>
<td>14.34</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>3.87</td>
<td>5.58</td>
<td>15.87</td>
<td>23.10</td>
<td>3.97</td>
<td>30.56</td>
</tr>
<tr>
<td>5</td>
<td>14.81</td>
<td>8.06</td>
<td>16.83</td>
<td>24.40</td>
<td>16.71</td>
<td>29.97</td>
</tr>
<tr>
<td>10</td>
<td>24.72</td>
<td>8.57</td>
<td>16.84</td>
<td>25.17</td>
<td>28.97</td>
<td>28.59</td>
</tr>
</tbody>
</table>

-- : not detected
Table 15. TMDSC data of C6 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3°C/min with a period of 40 s. All temperature in °C.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>Total heat flow</th>
<th>Reversing heat flow</th>
<th>Nonreversing heat flow</th>
<th>Crystallization Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R</td>
<td>R</td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>178.5</td>
<td>206.0</td>
<td>--</td>
<td>206.9</td>
</tr>
<tr>
<td>2</td>
<td>162.9</td>
<td>201.3</td>
<td>shoulder</td>
<td>201.2</td>
</tr>
<tr>
<td>5</td>
<td>157.3</td>
<td>198.4</td>
<td>206.0</td>
<td>198.7</td>
</tr>
<tr>
<td>10</td>
<td>141.0</td>
<td>shoulder</td>
<td>205.6</td>
<td>196.4</td>
</tr>
</tbody>
</table>

-- : not detected
** : not obvious

Table 16. TMDSC data of C6 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3 °C/min with a period of 40 s, including heats of melting and crystallization.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>H_{exo,NR}</th>
<th>H_{endo,NR}</th>
<th>H_{exo,R}</th>
<th>H_{endo,R}</th>
<th>H_{exo,total}</th>
<th>H_{endo,total}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>23.32</td>
<td>13.35</td>
<td>--</td>
<td>37.04</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>**</td>
<td>13.01</td>
<td>19.74</td>
<td>--</td>
<td>32.14</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-2.69</td>
<td>7.27</td>
<td>23.17</td>
<td>-1.00</td>
<td>28.92</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-4.60</td>
<td>7.14</td>
<td>26.19</td>
<td>-1.77</td>
<td>28.75</td>
<td></td>
</tr>
</tbody>
</table>

-- : not detected
** : not obvious
**Table 17.** TMDSC data of C7 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3 °C/min with a period of 40 s. All temperature in °C.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>Total heat flow</th>
<th>Reversing heat flow</th>
<th>Nonreversing heat flow</th>
<th>Crystallization Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>□</td>
<td>□</td>
<td>□ R</td>
<td>□ R</td>
</tr>
<tr>
<td>1</td>
<td>189.0</td>
<td>214.3</td>
<td>-- shoulder</td>
<td>214.6</td>
</tr>
<tr>
<td>2</td>
<td>182.7</td>
<td>211.5</td>
<td>-- shoulder</td>
<td>211.9</td>
</tr>
<tr>
<td>5</td>
<td>170.9</td>
<td>208.1</td>
<td>214.1 ** shoulder</td>
<td>208.6</td>
</tr>
<tr>
<td>10</td>
<td>--</td>
<td>207.0</td>
<td>213.0 ** shoulder</td>
<td>206.8</td>
</tr>
<tr>
<td>20</td>
<td>--</td>
<td>shoulder</td>
<td>212.4</td>
<td>202.8</td>
</tr>
</tbody>
</table>

-- : not detected  
** : not obvious

**Table 18.** TMDSC data of C7 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3°C/min with a period of 40 s, including heats of melting and crystallization.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>□&lt;sup&gt;H&lt;/sup&gt;&lt;sub&gt;exo,NR&lt;/sub&gt;</th>
<th>□&lt;sup&gt;H&lt;/sup&gt;&lt;sub&gt;endo,NR&lt;/sub&gt;</th>
<th>□&lt;sup&gt;H&lt;/sup&gt;&lt;sub&gt;endo,R&lt;/sub&gt;</th>
<th>□&lt;sup&gt;H&lt;/sup&gt;&lt;sub&gt;exo,total&lt;/sub&gt;</th>
<th>□&lt;sup&gt;H&lt;/sup&gt;&lt;sub&gt;endo,total&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>23.45</td>
<td>15.67</td>
<td>--</td>
<td>39.18</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>17.96</td>
<td>20.14</td>
<td>--</td>
<td>38.17</td>
</tr>
<tr>
<td>5</td>
<td>-0.87</td>
<td>10.18</td>
<td>25.30</td>
<td>--</td>
<td>35.80</td>
</tr>
<tr>
<td>10</td>
<td>-8.53</td>
<td>6.48</td>
<td>29.02</td>
<td>-3.63</td>
<td>28.67</td>
</tr>
<tr>
<td>20</td>
<td>-9.13</td>
<td>6.49</td>
<td>35.89</td>
<td>-1.41</td>
<td>31.42</td>
</tr>
</tbody>
</table>

-- : not detected  
** : not obvious
Table 19. TMDSC data of C8 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3 °C/min with a period of 40 s. All temperature in °C.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>Total heat flow</th>
<th>Reversing heat flow</th>
<th>Nonreversing heat flow</th>
<th>Crystallization Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Θ</td>
<td>Δ</td>
<td>Θ</td>
<td>Θ</td>
</tr>
<tr>
<td>1</td>
<td>**</td>
<td>235.9</td>
<td>241.6</td>
<td>shoulder</td>
</tr>
<tr>
<td>2</td>
<td>**</td>
<td>232.3</td>
<td>242.1</td>
<td>shoulder</td>
</tr>
<tr>
<td>5</td>
<td>--</td>
<td>--</td>
<td>241.6</td>
<td>**</td>
</tr>
<tr>
<td>10</td>
<td>--</td>
<td>--</td>
<td>241.6</td>
<td>**</td>
</tr>
<tr>
<td>20</td>
<td>(105.5)</td>
<td>--</td>
<td>241.7</td>
<td>--</td>
</tr>
</tbody>
</table>

-- : not detected
** : not obvious
( ) : cold crystallization

Table 20. TMDSC data of C8 copolyester that crystallized nonisothermally from the molten state at different cooling rate, at a heating rate of 3 °C/min with a period of 40 sec, including heats of melting and crystallization.

<table>
<thead>
<tr>
<th>Cooling rate (°C/min)</th>
<th>$\Delta H_{exo, NR}$</th>
<th>$\Delta H_{endo, NR}$</th>
<th>$\Delta H_{endo, R}$</th>
<th>$\Delta H_{exo, total}$</th>
<th>$\Delta H_{endo, total}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-3.54</td>
<td>5.76</td>
<td>46.28</td>
<td>--</td>
<td>48.63</td>
</tr>
<tr>
<td>2</td>
<td>-15.82</td>
<td>5.36</td>
<td>56.01</td>
<td>--</td>
<td>47.15</td>
</tr>
<tr>
<td>5</td>
<td>-26.11</td>
<td>6.81</td>
<td>61.61</td>
<td>--</td>
<td>41.60</td>
</tr>
<tr>
<td>10</td>
<td>-33.16</td>
<td>5.53</td>
<td>67.87</td>
<td>-0.74</td>
<td>41.50</td>
</tr>
<tr>
<td>20</td>
<td>-36.02</td>
<td>4.86</td>
<td>74.34</td>
<td>-2.48</td>
<td>41.35</td>
</tr>
</tbody>
</table>

-- : not detected
** : not obvious
Table 21. Crystallographic Data for PET and PTT.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>PET&lt;sup&gt;52&lt;/sup&gt;</th>
<th>PTT&lt;sup&gt;52&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>single crystal</td>
<td>fiber&lt;sup&gt;50&lt;/sup&gt;WAXD</td>
</tr>
<tr>
<td>crystal system</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>$P\bar{1}$</td>
<td>$P\bar{1}$</td>
</tr>
<tr>
<td>cell parameter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.56</td>
<td>4.64</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>5.94</td>
<td>6.23</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>10.75</td>
<td>18.64</td>
</tr>
<tr>
<td>$\alpha$ (deg.)</td>
<td>98.5</td>
<td>98.4</td>
</tr>
<tr>
<td>$\beta$ (deg.)</td>
<td>118.0</td>
<td>93.0</td>
</tr>
<tr>
<td>$\gamma$ (deg.)</td>
<td>112.0</td>
<td>111.1</td>
</tr>
</tbody>
</table>

Table 22. Avrami parameters of Poly[(ethylene)-<i>co</i>-(trimethylene terephthalate)]s

<table>
<thead>
<tr>
<th>Copolyester</th>
<th>Avrami Parameter</th>
<th>Cooling rate (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>1.0</td>
</tr>
<tr>
<td>C2(245°C)</td>
<td>$n$</td>
<td>4.36</td>
</tr>
<tr>
<td></td>
<td>$k'$</td>
<td>$3.45 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>$t_{1/2}$</td>
<td>391.2</td>
</tr>
<tr>
<td>C2(240°C)</td>
<td>$n$</td>
<td>3.93</td>
</tr>
<tr>
<td></td>
<td>$k'$</td>
<td>$6.93 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>$t_{1/2}$</td>
<td>350</td>
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<tr>
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<td>$n$</td>
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</tr>
<tr>
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<td>$k'$</td>
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</tr>
<tr>
<td></td>
<td>$t_{1/2}$</td>
<td>1032.1</td>
</tr>
<tr>
<td>C8(270°C)</td>
<td>$n$</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>$k'$</td>
<td>$1.35 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$t_{1/2}$</td>
<td>876.5</td>
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$k'$: the corrected rate constant of crystallization
$t_{1/2}$ (sec.): the crystallization half-time

Table 23. The melting temperature ($T_m$) and annealing temperature ($T_a$) for uniaxially oriented copolyester preparation.

<table>
<thead>
<tr>
<th>Copolyester</th>
<th>$T_m$ (°C)</th>
<th>$T_a$ (°C)</th>
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<tr>
<td>C2</td>
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<td>180</td>
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<tr>
<td>C3</td>
<td>200</td>
<td>140</td>
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<tr>
<td>C4</td>
<td>185</td>
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<td>140</td>
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<tr>
<td>C7</td>
<td>225</td>
<td>150</td>
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<tr>
<td>C8</td>
<td>260</td>
<td>180</td>
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Table 24. Observed and calculated X-ray spacings of PTT, PET and their copolyesters

<table>
<thead>
<tr>
<th>l</th>
<th>h</th>
<th>k</th>
<th>l</th>
<th>(d_{hkl}^a)</th>
<th>(d_{observed}^a)</th>
<th>Powder X-ray diffraction</th>
<th>Fiber X-ray diffraction</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PTT 9/91 34/66 38/62</td>
<td>PET 91/9 78/22 72/28</td>
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<tr>
<td>l=0</td>
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<td>1</td>
<td>0</td>
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<td>5.62 5.59</td>
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<td>1</td>
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<td>0</td>
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<td></td>
<td>4.07 4.03</td>
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<td>3.54</td>
<td>3.58 3.59</td>
<td>3.62 3.37 3.39</td>
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<tr>
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<td>0</td>
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<td>3.21 3.23</td>
<td>3.24 3.26</td>
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<td>3.16</td>
<td></td>
<td></td>
<td>2.88 2.91</td>
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\(a\) Indexing and spacings calculated for a triclinic system of cell parameter \(a_0 = 4.63(7) \text{ Å}, \ b_0 = 6.26(6) \text{ Å}, \ c_0 = 18.64 \text{ Å}, \ \alpha = 98.4^\circ, \ \beta = 93.0^\circ, \ \text{and} \ \gamma = 111.1^\circ.\)

\(b\) Indexing and spacings calculated for a triclinic system of cell parameter \(a_0 = 4.56 \text{ Å}, \ b_0 = 5.94 \text{ Å}, \ c_0 = 10.75 \text{ Å}, \ \alpha = 98.5^\circ, \ \beta = 98.5^\circ, \ \text{and} \ \gamma = 98.5^\circ.\)
Figure 1. DSC thermograms at a heating rate of 80°C/min for C2 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.

Figure 2. DSC thermograms at a heating rate of 80°C/min for C2 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.
**Figure 3.** DSC nonisothermal crystallization curves of C2 copolyester at various cooling rates. (Sample was preheated from room temperature up to 252°C at 20°C/min and maintained at 252°C for 5 min).

**Figure 4.** Plots of relative crystallinity $X_T$ versus crystallization temperature for C2 copolyester crystallized nonisothermally at various cooling rates.
**Figure 5.** Plots of relative crystallinity $X_T$ versus crystallization time for C2 copolyester crystallized nonisothermally at various cooling rates.

**Figure 6.** Plots of $\log[-\ln(1-X_T)]$ versus $\log R$ at indicated temperatures for C2 copolyester crystallized nonisothermally at various cooling rates. (Sample was preheated from room temperature up to 252 °C at 20°C/min and maintained at 252°C for 5 min).
**Figure 7.** Plots of log[-ln(1 - $X_f$)] versus log$R$ at indicated temperatures for C2 copolyester crystallized nonisothermally at various cooling rates. (Sample was preheated from room temperature up to 245°C at 20°C/min and maintained at 245°C for 5 min).

**Figure 8.** Plots of log[-ln(1 - $X_f$)] versus log$R$ at indicated temperatures for C2 copolyester crystallized nonisothermally at various cooling rates. (Sample was preheated from room temperature up to 240°C at 20°C/min and maintained at 240°C for 5 min).
**Figure 9.** Avrami plots of relative crystallinity $X_T$ for C2 copolyester crystallized nonisothermally at various cooling rates.

**Figure 10.** DSC thermograms at a heating rate of 50°C/min. for the melt-crystallized C2 samples cooled from melting state at various cooling rates indicated in the figure.
**Figure 11.** Total heat flow of TMDSC data at a heating rate of 2°C/min and a period of 40 sec for C2 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

**Figure 12.** Reversing heat flow of TMDSC data at a heating rate of 2°C/min and a period of 40 sec for C2 specimens crystallized nonisothermally at various cooling rates indicated in the figure.
Figure 13. Non-reversing heat flow of TMDSC data at a heating rate of 2°C/min and a period of 40 sec for C2 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

Figure 14. WAXD powder pattern of C2 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 180~204°C.
Figure 15. WAXD powder pattern of C2 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 183~207°C.

Figure 16. HTWAXD powder pattern of C2 copolyester crystallized isothermally at 212°C for 24 h.
**Figure 17.** DSC thermograms at a heating rate of 80°C/min for C3 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.

**Figure 18.** DSC thermograms at a heating rate of 80°C/min for C3 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.
Figure 19. DSC nonisothermal crystallization curves of C3 copolyester at various cooling rates. (Sample was preheated from room temperature up to 215°C at 20°C/min and maintained at 215°C for 5 min).

Figure 20. Plots of relative crystallinity $X_T$ versus crystallization temperature for C3 copolyester crystallized nonisothermally at various cooling rates.
**Figure 21.** Plots of relative crystallinity $X_T$ versus crystallization time for C3 copolyester crystallized nonisothermally at various cooling rates.

**Figure 22.** Plots of $\log[-\ln(1 - X_T)]$ versus $\log R$ at indicated temperature for C3 copolyester crystallized nonisothermally at various cooling rates.
Figure 23. Avrami plots of relative crystallinity $X_T$ for C3 copolyester crystallized nonisothermally at various cooling rates.

Figure 24. DSC thermograms at a heating rate of 50°C/min for the melt-crystallized C3 samples cooled from melting state at various cooling rates indicated in the figure.
Figure 25. Total heat flow of TMDSC data at a heating rate of 3\(^\circ\)C/min and a period of 40 sec for C3 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

Figure 26. Reversing heat flow of TMDSC data at a heating rate of 3\(^\circ\)C/min and a period of 40 sec for C3 specimens crystallized nonisothermally at various cooling rates indicated in the figure.
**Figure 27.** Non-reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C3 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

**Figure 28.** WAXD powder pattern of C3 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 126~166°C.
**Figure 29.** WAXD powder pattern of C3 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 130~170°C.

**Figure 30.** HTWAXD powder pattern of C3 copolyester crystallized isothermally at 174°C for 12 h. The asterisk (*) indicates the major reflection in the diffraction peak.
Figure 31. DSC thermograms at a heating rate of 80°C/min for C4 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.

Figure 32. DSC thermograms at a heating rate of 80°C/min for C4 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.
**Figure 33.** DSC nonisothermal crystallization curves of C4 copolyester at various cooling rates. (Sample was preheated from room temperature up to 192°C at 20°C/min and maintained at 192°C for 5 min).

**Figure 34.** Plots of relative crystallinity $X_T$ versus crystallization temperature for C4 copolyester crystallized nonisothermally at various cooling rates.
Figure 35. Plots of relative crystallinity $X_T$ versus crystallization time for C4 copolyester crystallized nonisothermally at various cooling rates.

Figure 36. Plots of $\log[-\ln(1-X_T)]$ versus $\log R$ at indicated temperature for C4 copolyester crystallized nonisothermally at various cooling rates.
Figure 37. Avrami plots of relative crystallinity $X_T$ for C4 copolyester crystallized nonisothermally at various cooling rates.

Figure 38. DSC thermograms at a heating rate of 50°C/min for the melt-crystallized C4 samples cooled from melting state at various cooling rates indicated in the figure.
Figure 39. Total heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C4 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

Figure 40. Reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C4 specimens crystallized nonisothermally at various cooling rates indicated in the figure.
**Figure 41.** Non-reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C4 crystallized nonisothermally at various cooling rates indicated in the figure.

**Figure 42.** WAXD powder pattern of C4 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 120~160°C.
**Figure 43.** WAXD powder pattern of C4 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 124~156°C.

**Figure 44.** HTWAXD powder pattern of C4 copolyester crystallized isothermally at 164°C for 12 h. The asterisk (*) indicates the major reflection in the diffraction peak.
Figure 45. DSC thermograms at a heating rate of 80°C/min for C6 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.

Figure 46. DSC nonisothermal crystallization curves of C6 copolyester at various cooling rates. (Sample was preheated from room temperature up to 228°C at 20°C/min and maintained at 228°C for 5 min).
Figure 47. Plots of relative crystallinity $X_T$ versus crystallization temperature for C6 copolyester crystallized nonisothermally at various cooling rates.

Figure 48. Plots of relative crystallinity $X_T$ versus crystallization time for C6 copolyester crystallized nonisothermally at various cooling rates.
Figure 49. Plots of log[-ln(1-\(X_T\))] versus log\(R\) at indicated temperature for C6 copolyester crystallized nonisothermally at various cooling rates.

Figure 50. Avrami plots of relative crystallinity \(X_T\) for C6 copolyester crystallized nonisothermally at various cooling rates.
**Figure 51.** DSC thermograms at a heating rate of 50°C /min for the melt-crystallized C6 samples cooled from melting state at various cooling rates indicated in the figure.

**Figure 52.** Total heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C6 crystallized nonisothermally at various cooling rates indicated in the figure.
Figure 53. Reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C6 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

Figure 54. Non-reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C6 specimens crystallized nonisothermally at various cooling rates indicated in the figure.
Figure 55. WAXD powder pattern of C6 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 136~184°C.

Figure 56. WAXD powder pattern of C6 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 140~188°C.
Figure 57. DSC nonisothermal crystallization curves of C7 copolyester at various cooling rates (sample was preheated from room temperature up to 234°C at 20°C/min and maintained at 234°C for 5 min).

Figure 58. Plots of relative crystallinity $X_T$ versus crystallization temperature for C7 copolyester crystallized nonisothermally at various cooling rates.
Figure 59. Plots of relative crystallinity \( X_T \) versus crystallization time for C7 copolyesters crystallized nonisothermally at various cooling rates.

Figure 60. Plots of \( \log[-\ln(1-X_T)] \) versus \( \log R \) at indicated temperature for C7 copolyesters crystallized nonisothermally at various cooling rates.
Figure 61. Avrami plots of relative crystallinity $X_T$ for C7 copolyester crystallized nonisothermally at various cooling rates.

Figure 62. DSC thermograms at a heating rate of 50°C/min for the melt-crystallized C7 samples cooled from melting state at various cooling rates indicated in the figure.
**Figure 63.** Total heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C7 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

**Figure 64.** Reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C7 crystallized nonisothermally at various cooling rates indicated in the figure.
Figure 65. Non-reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C7 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

Figure 66. WAXD powder pattern of C7 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 144~192°C.
Figure 67. WAXD powder pattern of C7 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 148~188°C.

Figure 68. DSC thermograms at a heating rate of 80°C/min for C8 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.
Figure 69. DSC thermograms at a heating rate of 80°C/min for C8 copolyester specimens isothermally crystallized at various temperatures indicated in the figure.

Figure 70. DSC nonisothermal crystallization curves of C8 copolyester at various cooling rates. (Sample was preheated from room temperature up to 276°C at 20°C/min and maintained at 276°C for 5 min).
**Figure 71.** Plots of relative crystallinity $X_T$ versus crystallization temperature for C8 copolyester crystallized nonisothermally at various cooling rates.

**Figure 72.** Plots of relative crystallinity $X_T$ versus crystallization time for C8 copolyester crystallized nonisothermally at various cooling rates.
Figure 73. Plots of log[-ln(1 - \(X_{T}\))] versus log\(R\) at indicated temperature for C8 copolyester crystallized nonisothermally at various cooling rates. (Sample was preheated from room temperature up to 245°C at 20°C/min and maintained at 276°C for 5 min).

Figure 74. Plots of log[-ln(1 - \(X_{T}\))] versus log\(R\) at indicated temperature for C8 copolyester crystallized nonisothermally at various cooling rates. (Sample was preheated from room temperature up to 270°C at 20°C/min and maintained at 270°C for 5 min).
Figure 75. Plots of $\log[-\ln(1 - X_T)]$ versus $\log R$ at indicated temperature for C8 copolyester crystallized nonisothermally at various cooling rates. (Sample was preheated from room temperature up to 265°C at 20°C/min and maintained at 265°C for 5 min).

Figure 76. Avrami plots of relative crystallinity $X_T$ for C8 copolyester crystallized nonisothermally at various cooling rates.
Figure 77. DSC thermograms at a heating rate of 50°C/min for the melt-crystallized C8 samples cooled from melting state at various cooling rates indicated in the figure.

Figure 78. Total heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C8 specimens crystallized nonisothermally at various cooling rates indicated in the figure.
**Figure 79.** Reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C8 specimens crystallized nonisothermally at various cooling rates indicated in the figure.

**Figure 80.** Non-reversing heat flow of TMDSC data at a heating rate of 3°C/min and a period of 40 sec for C8 crystallized nonisothermally at various cooling rates indicated in the figure.
**Figure 81.** WAXD powder pattern of C8 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 176~216°C.

**Figure 82.** WAXD powder pattern of C8 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 180~220°C.
Figure 83. DSC heating (A) and cooling (B) thermograms for melt-quenched copolyesters of (a) PTT; (b) PT91/ET9; (c) PT66/ET34; (d) PT62/ET38; (e) PT50/ET50; (f) PT28/ET72; (g) PT22/ET78; (h) PT9/ET91; (i) PET.
Figure 84. X-ray diffraction patterns of the melt-crystallized copolyesters of (a) PTT; (b) PT91/ET9; (c) PT66/ET34; (d) PT62/ET38; (e) PT50/ET50; (f) PT28/ET72; (g) PT22/ET78; (h) PT9/ET91; (i) PET. The asterisk (*) indicates the major reflection in the diffraction peak.
Figure 85. Changes of d spacings for the melt-crystallized copolyester as a function of the copolymer composition.

Figure 86. WAXD powder pattern of C5 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 115~145°C.
**Figure 87** IR spectra of C5 copolyester after the sample was crystallized isothermally for different time at the indicated temperature ranging from 115~145°C.

**Figure 88.** IR spectra of C5 PET/PTT copolyester; upper trace, crystalline sample; lower trace, amorphous sample.
Figure 89. Transmission pinhole photographs of uniaxially oriented copolymer of (a) PT91/ET9; (b) PT66/ET34; (c) PT62/ET38; (d) PT50/ET50. The fiber axis is vertical.
Figure 90. Transmission pinhole photographs of Uniaxially oriented copolymer of (e) PT28/ET72; (f) PT22/ET78; (g) PT9/ET91 copolymer. The fiber axis is vertical.