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European Polymer Journal 40 (2004) 599–608

EUROPEAN  
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# Multiple melting behavior in isothermally crystallized poly(trimethylene terephthalate)

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Received 20 March 2003; received in revised form 26 October 2003; accepted 6 November 2003

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## Abstract

Melting behavior of poly(trimethylene terephthalate) (PTT) after isothermal crystallization from the melt state was studied using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) techniques. The subsequent melting thermograms for PTT isothermally crystallized within the temperature range of 182–215 °C exhibited triple (for crystallization temperatures lower than ≈192 °C), double (for crystallization temperatures greater than ≈192 °C but lower than ≈210 °C), or single (for crystallization temperatures greater than ≈210 °C) endothermic melting phenomenon. These peaks were denoted peaks I, II, and III for low-, middle-, and high-temperature melting endotherms, respectively. For the triple melting phenomenon, it was postulated that the occurrence of peak I was a result of the melting of the primary crystallites, peak II was a result of the melting of recrystallized crystallites, and peak III was a result of the melting of the recrystallized crystallites of different stabilities. In addition, determination of the equilibrium melting temperature  $T_m^0$  for this PTT resin according to the linear and non-linear Hoffmann–Weeks extrapolation provided values of 243.6 and 277.6 °C, respectively.

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**Keywords:** Poly(trimethylene terephthalate); Multiple melting behavior; Equilibrium melting behavior

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## 1. Introduction

In 1941, a new type of linear aromatic polyester, poly(trimethylene terephthalate) (PTT), was successfully synthesized by Whinfield and Dickson [1], but it was not available commercially then due to the high production cost of a key reactant, 1,3-propanediol. With a breakthrough in the synthesis of 1,3-propanediol at a much lower cost, PTT is now commercially available and has been produced by Shell Chemicals under the tradename Corterra™. PTT has properties in between those of poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), with an unusual combination of

the outstanding properties of PET and processing characteristics of PBT. These make PTT highly suitable for uses in fiber, film and engineering thermoplastic applications.

Recently, our group reported isothermal bulk crystallization and subsequent melting behavior in PTT using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) techniques [2]. It was found that the subsequent DSC thermograms exhibited either two or three distinct melting endotherms, depending on the temperature at which the samples were crystallized. Under the conditions studied [2], the triple melting behavior of PTT was preliminarily postulated to be a result of the melting of the primary crystallites, the melting of the recrystallized crystallites, and the melting of the recrystallized crystallites of different stabilities. Although the aforementioned postulation was satisfactory in describing our previous results, further

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investigation is necessary to gain a complete understanding on the true origin of the multiple melting behavior observed in isothermally crystallized PTT.

Multiple melting is not an exclusive phenomenon for PTT. A number of investigators reported similar observations on a number of semicrystalline polymers, including some flexible polymers: polyethylene [3,4], isotactic polypropylene (i-PP) [5,6], syndiotactic polypropylene (s-PP) [7], *trans*-1,4-polyisoprene [8], and poly(butylene succinate) [9], and some semistiff polymers: aliphatic polyamides [10], isotactic polystyrene (i-PS) [11], syndiotactic polystyrene and its blends [12], poly(ethylene terephthalate) [13–15], poly(butylene terephthalate) [16–18], poly(phenylene sulfide) [19], and poly(aryl ether ether ketones) [20,21].

A number of hypotheses were proposed to explain the phenomenon. In the studies of isothermal crystallization of semicrystalline polymers under quiescent conditions (i.e., crystallization is only a function of temperature), the multiple melting behavior for these polymers may be designated as being the result of one of the following reasons: the presence of two (or more) crystal modifications [5,8], the presence of two (or more) crystalline morphologies [16], the presence of two populations of crystal lamellae of different stabilities [22–25], and the simultaneous melting, recrystallization, and remelting of the lamellae initially formed at the crystallization conditions [13,26–28]. Among these models, the simultaneous melting–recrystallization–remelting and the dual-lamellar population models seem to have received much attention in explaining the multiple melting behavior in various semicrystalline polymers that do not exhibit multiple crystal modifications upon crystallizing at the crystallization conditions studied.

The simultaneous melting–recrystallization–remelting model [13,26–28] hypothesizes that the primary lamellae formed at the crystallization temperature  $T_c$  undergo a partial melting process that gives rise to an observation of the low-melting endotherm (usually observed at  $\approx 10$  °C above the  $T_c$ ). During the heating scan, the partially melted material undergoes a simultaneous process of recrystallization into thicker and more perfect lamellae that, upon melting, gives rise to the observation of the high-melting endotherm. This postulated model was primarily based on the observation that the magnitude and position of the low endotherm is heating rate dependent. The suitability of the model was questioned by the experimental findings that the occurrence of the high-melting endotherm precedes that of the low-temperature endotherm [23,29,30], which clearly contradicts the assignment of the low endotherm to the partial melting of the primary lamellae as postulated in this model.

The dual-lamellar population model [22–25] hypothesizes that a bimodal distribution of lamellae of different stabilities exists within crystalline aggregates formed at the crystallization conditions studied, and the melting of

the thin and the thick lamellae gives rise to the appearance of the low- and high-temperature endotherms, respectively. The two variants of this model [31] are the dual-lamellar stack model [21,24,30,32] and the lamellar insertion model [25]. According to the dual-lamellar stack model, the distribution of the stacks of thick and thin lamellae is such that they exist in different stacks, while, in the lamellar insertion model, they coexist in the same stacks with the thin lamellae distributing between two thick lamellae. The applicability of these two variants in describing the experimental data is controversial and is very dependent on the experimental conditions and, perhaps, on the technique used to obtain the data.

Chung et al. [33] and Wu and Woo [34,35] reported the multiple melting phenomenon for isothermally crystallized PTT, similar to what has been found in this work. Chung et al. [33], however, attributed the occurrence of peak I to the recrystallization during the reheating scan in DSC and peaks II and III to the melting of the primary crystallites of different stabilities. On the contrary to Chung et al. [33], Wu and Woo [34] designated the occurrence of peak I to the melting of the primary crystallites. Very recently, Wu and Woo [35] suggested that the multiple melting phenomenon in PTT correlated with the ringed spherulites being formed at different  $T_c$ 's. They reported that, for PTT samples exhibiting ringed spherulites (i.e., isothermally crystallized at  $T_c$ 's ranging from 150 to 215 °C), either double or triple endothermic peaks was observed, while, for PTT samples exhibiting non-ringed spherulites (i.e., isothermally crystallized at  $T_c$ 's greater than 220 °C), only single endothermic peak was observed.

Two different extrapolative methods have been used to arrive at an estimate of the equilibrium melting temperature  $T_m^0$  of PTT. The linear Hoffman–Weeks extrapolation (LHW) was used to obtain the  $T_m^0$  value of PTT as being  $\approx 237$  [36], 244 [37], 245 [34], 248 [38], and 252 °C [33], while the non-linear Hoffman–Weeks extrapolation (NLHW) arrived at the  $T_m^0$  value of  $\approx 273$  °C [34].

In the present contribution, differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) techniques were used to investigate multiple melting behavior of PTT after isothermal crystallization from the melt state at various crystallization temperatures, ranging from 182 to 215 °C. The equilibrium melting temperature  $T_m^0$  of this particular PTT resin was also estimated based on the linear and non-linear Hoffman–Weeks extrapolative methods.

## 2. Experimental detail

### 2.1. Materials

Poly(trimethylene terephthalate) (PTT) was supplied in pellet form by Shell Chemicals (USA) (Corterra

CP509201). The weight- and number-average molecular weights for this resin were determined by size-exclusion chromatography (SEC) technique by Dr. Hoe H. Chuah and his colleagues of Shell Chemicals (USA) to be  $\approx 78,100$  and  $34,700$  Daltons, respectively.

## 2.2. Sample preparation

PTT resin was dried in a vacuum oven at  $140\text{ }^{\circ}\text{C}$  for 5 h prior to further use. A film of approximately  $200\text{ }\mu\text{m}$  in thickness was melted-pressed at  $260\text{ }^{\circ}\text{C}$  in a compression molding machine (Wabash, V50H) under an applied pressure of  $4.62 \times 10^2\text{ MN m}^{-2}$ . After 5 min holding time, the film was taken out and allowed to cool at the ambient condition down to room temperature between two metal platens. This treatment assumes that previous thermomechanical history was essentially erased, and provided a standard crystalline memory condition for the as-prepared film.

## 2.3. Differential scanning calorimetry measurements

A DSC (Perkin-Elmer, DSC-7), equipped with an intracooling unit capable of maintaining the temperature of the jacket at  $-40\text{ }^{\circ}\text{C}$ , was used to investigate the multiple melting behavior of PTT. Calibration for the temperature scale was carried out using a pure indium standard ( $T_m^0 = 156.6\text{ }^{\circ}\text{C}$  and  $\Delta H_f^0 = 28.5\text{ J g}^{-1}$ ) on every other run to ensure accuracy and reliability of the data obtained. To minimize thermal lag between polymer sample and the DSC furnace, each sample holder was loaded with a disc-shaped sample weighing around  $8.0 \pm 0.3\text{ mg}$ , cut from the as-prepared film using a hand-held hole-puncher. Each sample was used only once and all the runs were carried out under nitrogen atmosphere to prevent extensive thermal degradation.

The experiment started with heating each sample from  $40\text{ }^{\circ}\text{C}$  at a heating rate of  $80\text{ }^{\circ}\text{C min}^{-1}$  to a desired fusion temperature  $T_f$  of  $280\text{ }^{\circ}\text{C}$  for a holding period of 5 min. After this period, each sample was rapidly cooled (i.e., at a cooling of  $\approx 200\text{ }^{\circ}\text{C min}^{-1}$ ) from  $T_f$  to a desired crystallization temperature  $T_c$  ranging from  $182$  to  $215\text{ }^{\circ}\text{C}$ , where it was held until crystallization process was considered complete (when no significant change in the heat flow as a function of time was further observed). All of the subsequent melting endotherms, after isothermal crystallization from the melt state at different temperatures, were recorded for further analysis.

## 2.4. Crystal structure and crystallinity measurements

Wide-angle X-ray diffraction (WAXD) technique was used to determine the crystal modification of PTT samples which were prepared in the same conditions prescribed in Section 2.3 (viz. after the samples were completely crystallized at a desired crystallization tem-

perature, they were immediately quenched, without subsequent heating, to  $30\text{ }^{\circ}\text{C}$ ). Each sample was then taken out of the DSC sample holder and was pasted onto a glass X-ray sample holder, using vaseline as adhesive. The WAXD intensity pattern for each sample was recorded on an X-ray diffractometer (Rigaku, Rint 2000), equipped with a computerized data collection and analytical tools. The X-ray source ( $\text{CuK}\alpha$  radiation,  $\lambda = 1.54\text{ \AA}$ ) was operated at an applied voltage of  $40\text{ kV}$  and a filament current of  $30\text{ mA}$ .

## 3. Results and discussion

### 3.1. Dependence of subsequent melting endotherms on crystallization temperature

Fig. 1 illustrates subsequent melting endotherms ( $10\text{ }^{\circ}\text{C min}^{-1}$ ) for PTT samples isothermally melt-crystallized at various crystallization temperatures  $T_c$  ranging from  $182$  to  $215\text{ }^{\circ}\text{C}$ . Each sample was held at  $260\text{ }^{\circ}\text{C}$  for 5 min to ensure complete melting and was later quenched to the desired  $T_c$  at the highest achievable cooling rate allowed by the DSC (i.e.,  $\approx 200\text{ }^{\circ}\text{C min}^{-1}$ ). The total crystallization time required for completion of crystallization at each  $T_c$  varied and was found to be an increasing function of it (e.g.,  $\approx 2\text{ min}$  at  $T_c$  of  $182\text{ }^{\circ}\text{C}$  and  $\approx 8\text{ min}$  at  $T_c$  of  $198\text{ }^{\circ}\text{C}$ ). An earlier report provides a complete discussion of the bulk crystallization kinetics for this PTT resin [2].

According to Fig. 1, the subsequent melting thermograms illustrated exhibited triple (for  $T_c$ 's lower than  $\approx 192\text{ }^{\circ}\text{C}$ ), double (for  $T_c$ 's greater than  $\approx 192\text{ }^{\circ}\text{C}$  but lower than  $\approx 210\text{ }^{\circ}\text{C}$ ), or single (for  $T_c$ 's greater than

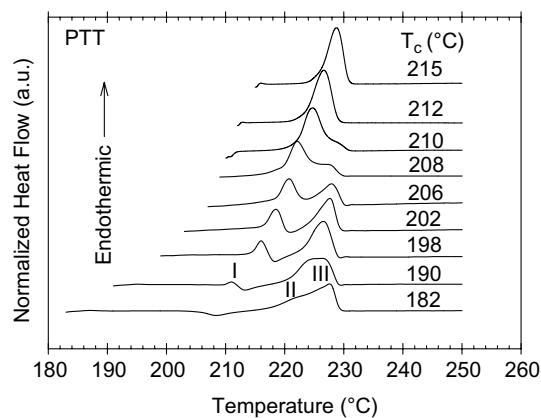


Fig. 1. Subsequent melting endotherms (recorded at  $10\text{ }^{\circ}\text{C min}^{-1}$ ) for PTT samples isothermally crystallized from the melt state at different crystallization temperatures. Peaks I, II, and III denoted the low-, middle-, and high-temperature melting endotherm, respectively.

$\approx 210$  °C) endothermic melting phenomenon. These endothermic peaks were labeled as I, II, and III for low-, middle-, and high-temperature melting endotherms, respectively. The peak temperature for these endotherms was therefore denoted as the low-melting peak temperature  $T_I$ , the middle-melting peak temperature  $T_{II}$  and the high-melting peak temperature  $T_{III}$  respectively. Quantitative information for all of the subsequent melting thermograms recorded is summarized in Table 1.

According to Table 1, peak I was only observed for samples isothermally crystallized at  $T_c$ 's greater than  $\approx 188$  °C, peak II was only observed for samples isothermally crystallized at  $T_c$ 's lower than  $\approx 210$  °C, and peak III was only observed for samples isothermally crystallized at  $T_c$ 's lower than  $\approx 192$  °C. Even though the positions of both peaks I and II steadily increased with increasing  $T_c$  the variation in the position of peak II, in comparison with that of peak I, with  $T_c$  was much less obvious. Unlike peaks I and II, changes in  $T_c$  did not affect the position of peak III at all. Apart from the position of these peaks with respect to the choice of  $T_c$  used to crystallize the sample, the enthalpic information, also listed in Table 1, suggests that peak I became more pronounced, while peak II became less pronounced, with increasing  $T_c$  and that peak III was not affected by changes in  $T_c$  at all.

Before going further, we must first investigate whether the multiple melting behavior observed in PTT (within the  $T_c$  range studied) was a result of the melting

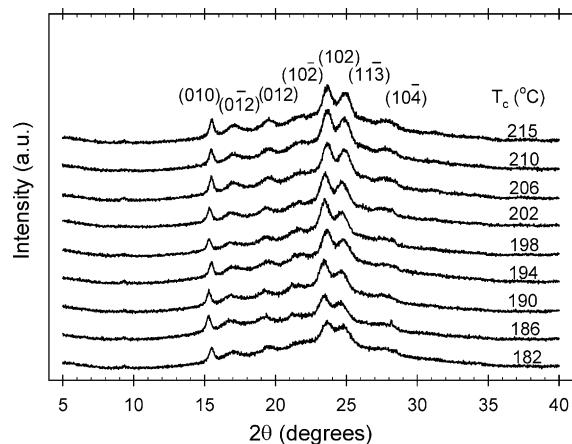


Fig. 2. Wide-angle X-ray diffractograms for PTT samples isothermally crystallized from the melt state at the different crystallization temperatures.

of crystals of different modifications. Fig. 2 shows WAXD patterns for PTT samples isothermally crystallized at  $T_c$ 's ranging from 182 to 215 °C. Qualitatively, all of the WAXD patterns exhibited seven characteristic peaks at the scattering angles  $2\theta$  of  $\approx 15.3^\circ$ ,  $16.8^\circ$ ,  $19.4^\circ$ ,  $21.8^\circ$ ,  $23.6^\circ$ ,  $24.6^\circ$  and  $27.3^\circ$ , corresponding to the reflection planes of  $(010)$ ,  $(0\bar{1}2)$ ,  $(012)$ ,  $(10\bar{2})$ ,  $(102)$ ,  $(1\bar{1}3)$ , and  $(10\bar{4})$ , respectively [39]. Since the positions of these characteristic peaks were not affected by the

Table 1

Variation of low-melting peak temperature  $T_I$ , middle-melting peak temperature  $T_{II}$ , high-melting peak temperature  $T_{III}$ , and enthalpy of fusion  $\Delta H_f$  for PTT measured at various crystallization temperatures  $T_c$

$T_c$ (°C)	$T_I$ (°C)	$\Delta H_{fI}$ (J g $^{-1}$ )	$T_{II}$ (°C)	$\Delta H_{fII}$ (J g $^{-1}$ )	$T_{III}$ (°C)	$\Delta H_{fIII+III}$ (J g $^{-1}$ )	Sum of $\Delta H_f$ (J g $^{-1}$ )
182	—	—	221.8	—	227.5	56.3	56.3
184	—	—	222.0	—	227.0	53.5	53.5
186	—	—	223.3	—	226.9	54.0	54.0
188	209.9	0.80	223.8	—	226.7	54.7	55.5
190	211.2	1.19	225.5	—	227.0	51.4	52.6
192	212.4	2.58	225.4	—	226.5	49.5	52.1
194	213.7	4.21	225.9	46.3	—	—	50.6
196	214.9	5.97	225.9	44.4	—	—	50.4
198	216.2	7.58	226.5	41.0	—	—	48.6
200	217.4	12.3	227.0	39.0	—	—	51.3
201	218.0	13.7	227.4	35.2	—	—	48.9
202	218.5	15.7	227.7	35.9	—	—	51.6
203	219.2	16.0	227.9	31.0	—	—	47.0
204	219.7	20.9	228.0	28.5	—	—	49.4
205	220.0	25.1	227.7	25.8	—	—	50.9
206	220.7	27.6	228.2	23.9	—	—	51.5
207	221.4	35.2	227.9	16.5	—	—	51.7
208	222.2	—	227.9	—	—	—	52.8
210	224.7	—	229.4	—	—	—	59.4
211	226.0	—	—	—	—	—	62.3
212	226.7	—	—	—	—	—	59.0
213	226.9	—	—	—	—	—	59.2
215	228.9	—	—	—	—	—	56.8

choice of  $T_c$  used, it is apparent that, within the  $T_c$  range studied, PTT crystallized in only one crystal modification (i.e., a triclinic unit cell with axes  $a = 4.64 \text{ \AA}$ ,  $b = 6.27 \text{ \AA}$  and  $c = 18.64 \text{ \AA}$ , angles  $\alpha = 98^\circ$ ,  $\beta = 90^\circ$ , and  $\gamma = 112^\circ$ , and space group  $P\bar{1}$  [40]). Evidently, the hypothesis of multiple crystal modifications as the source for the multiple melting behavior observed in PTT can be ruled out completely.

In s-PP, the triple melting endotherms were also observed in samples crystallized at “low” temperature [7]. The minor endotherm, located close to each corresponding  $T_c$ , was postulated to be the melting of the secondary crystallites formed at that  $T_c$ . The low-temperature melting peak was found to be the melting of the primary crystallites formed at  $T_c$ , and the high-temperature melting peak was a result of the melting of the crystallites recrystallized during a heating scan. The triple melting behavior observed in s-PP was therefore ascribed as contributions from melting of the secondary crystallites and their recrystallization, partial melting of the less stable fraction of the primary crystallites and their recrystallization, melting of the primary crystallites, and remelting of the recrystallized crystallites formed during the heating scan.

Based on the knowledge obtained for s-PP, preliminary postulation on the origin of the multiple melting behavior for PTT can now be offered. In PTT, the occurrence of the minor endotherm, characterizing the melting of secondary crystallites, was not so apparent, even though trace amount of such a peak was observed in the subsequent melting endotherms of samples isothermally crystallized at  $T_c$ 's lower than 190 °C. The occurrence of peak I was quite obvious due to the fact that it became more pronounced and shifted towards a higher temperature with increasing  $T_c$ , suggesting that peak I was likely a result of the melting of the primary crystallites. On the contrary, peak II became less pronounced and its position was not shifted so much with increasing  $T_c$ , suggesting that peak II might be only a result of the melting of the recrystallized crystallites during a heating scan. The occurrence of peak III was much less obvious, but it is logical at this point to postulate that peak III was a result of the melting of the recrystallized crystallites of different stabilities which might become prevalent at  $T_c$ 's lower than 192 °C. Further investigation proceeds in subsequent subsections.

### 3.2. Dependence of subsequent melting endotherms on crystallization time interval

It is a known fact that secondary crystallization is a very slow process and often lags behind primary crystallization. If the minor endotherm observed in subsequent melting scans of PTT was indeed attributed to the melting of the secondary crystals, one would expect

that it should not be present in subsequent melting endotherms recorded at early stages of crystallization (i.e., partial crystallization for short time intervals at a given  $T_c$ ). In order to test the validity of the hypothesis, separate experiments were carried out. In these experiments, PTT samples were partially crystallized for different time intervals at 182, 198, and 208 °C, respectively. Due to space limitation, only the results obtained for  $T_c$ 's of 182 and 208 °C are shown graphically.

Fig. 3 illustrates some representative DSC melting thermograms of PTT (recorded at  $20 \text{ ^\circ C min}^{-1}$ ) after isothermal crystallization at 182 °C for 0.5, 0.6, 0.7, 0.8, and 1.0 min and Fig. 4 shows some representative DSC melting thermograms of PTT (recorded at  $20 \text{ ^\circ C min}^{-1}$ ) after isothermal crystallization at 208 °C for 10.0, 12.5, 17.0, and 22.0 min, while Table 2 summarizes quantitative results obtained on all of the melting endotherms recorded. At 182 °C, a time interval of at least 0.3 min was required for a melting peak to be observed in the subsequent melting endotherm (not shown), while there were at least 0.5 and 1.5 min in the case of crystallization at 198 and 208 °C, respectively. For the first approximation, the time intervals of  $\approx 0.3$ , 0.5, and 1.5 min corresponded to the apparent induction time needed for stable crystallites to be observed at the respective  $T_c$ 's.

A thorough examination of these melting endotherms suggested that the occurrence of the secondary crystallization can be determined decisively. At 182 °C, the minor endotherm, located close to the  $T_c$ , was discernible after partial crystallization for at least 0.8 min, while, at 198 °C, the presence of the minor endothermic shoulders was clearly visible after partial crystallization for at least 4.5 min. At 208 °C, the minor endothermic shoulders were apparent on all of the subsequent melting endotherms observed. According to the data obtained for

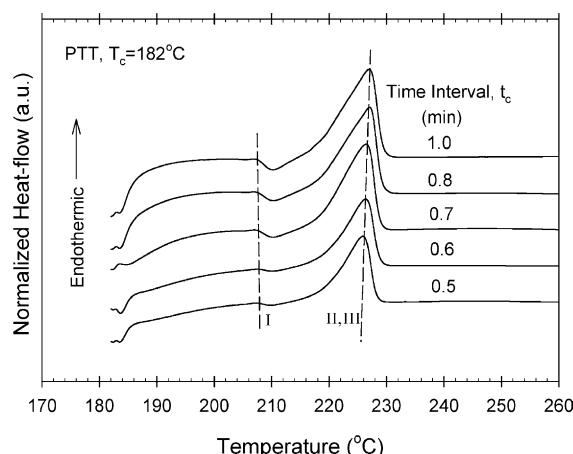


Fig. 3. Subsequent melting endotherms (recorded at  $20 \text{ ^\circ C min}^{-1}$ ) for PTT samples after partial crystallization at 182 °C for different time intervals as indicated.

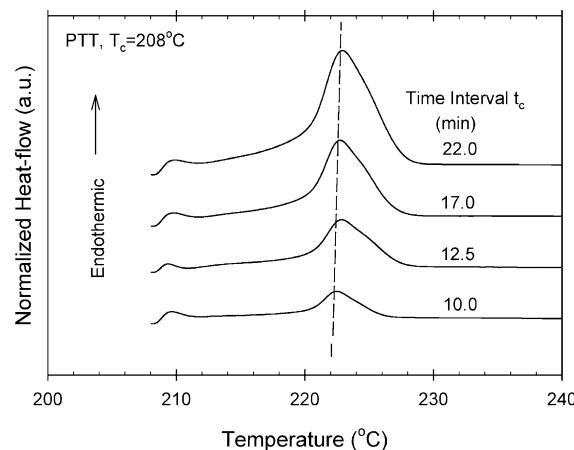


Fig. 4. Subsequent melting endotherms (recorded at  $20\text{ }^{\circ}\text{C min}^{-1}$ ) for PTT samples after partial crystallization at  $208\text{ }^{\circ}\text{C}$  for different time intervals as indicated.

partial crystallization at  $198$  and  $208\text{ }^{\circ}\text{C}$ , a general observation can be drawn in that the position where the minor endotherm was observed was located close to the  $T_c$ , where the sample was crystallized, and seemed to increase in its size and shift to a higher temperature with increasing crystallization time interval at  $T_c$ . This observation suggests that the existence of the minor endotherm corresponded to a contribution from a rather slow crystallization mechanism occurring at the  $T_c$ , which is most likely a result of the secondary crystallization. At this point, it is logical to establish that the minor endotherm and the peak I were caused by the melting of the secondary and primary crystallites formed at the  $T_c$ .

In addition to their use for determining the source of the minor endotherm, Figs. 3 and 4 provide us with additional information on the melting behavior of PTT in that the positions of peak I, which were taken as the melting endotherm of the primary crystallites formed at the  $T_c$ , were essentially unaffected by changes in the crystallization time intervals. The average values of peak I were  $216.9 \pm 0.2\text{ }^{\circ}\text{C}$  for samples crystallized at  $198\text{ }^{\circ}\text{C}$

and  $222.7 \pm 0.3\text{ }^{\circ}\text{C}$  for samples crystallized at  $208\text{ }^{\circ}\text{C}$ , while the average values of peak II were  $226.7 \pm 0.4\text{ }^{\circ}\text{C}$  for samples crystallized at  $198\text{ }^{\circ}\text{C}$  (see Table 2). According to the Gibbs–Thomson (GT) equation [41,42], a relationship exists between the observed melting temperature  $T_m$  and the lamellar thickness  $l_c$  of the crystallites:

$$T_m = T_m^0 \left( 1 - \frac{2\sigma_e}{\Delta H_f^0} \cdot \frac{1}{l_c} \right), \quad (1)$$

where  $T_m^0$  is the melting point of an infinitely thick crystal for the studied polymer and  $\sigma_e$  is the fold surface free energy. According to Eq. (1), the fact that the positions of the peak I were essentially constant during the crystallization process suggests that the average thickness of the primary crystallites formed at each  $T_c$  is essentially constant throughout the crystallization process. In other words, the results suggested that the primary crystallites formed at the  $T_c$  did not thicken during the course of crystallization.

### 3.3. Dependence of subsequent melting endotherms on heating rate

In previous subsections, the origin of the minor and the low-temperature melting endotherms (peak I) has been identified as the melting of the secondary and the primary crystallites formed at a  $T_c$ . Since it has earlier been postulated that the occurrence of peaks II and III might be a result of the melting of the recrystallized crystallites of two different stabilities, which were formed during a heating scan, the extent of the recrystallization process from the crystallizable materials due to the melting of the secondary and the primary crystallites significantly depends on the original  $T_c$  where these crystallites were formed, the chemical structure of the polymers studied, and the scanning rate used during the heating scan in the DSC. In addition, one can expect that the melting point of these recrystallized crystallites must be higher than that of the primary crystals formed at the  $T_c$ .

Table 2

Variation of low-melting peak temperature  $T_1$ , middle-melting peak temperature  $T_{II}$ , and enthalpy of fusion  $\Delta H_f$  for PTT measured at crystallization temperatures  $T_c$  of  $182$ ,  $198$ , and  $208\text{ }^{\circ}\text{C}$  for various crystallization time intervals

$T_c = 182\text{ }^{\circ}\text{C}$			$T_c = 198\text{ }^{\circ}\text{C}$					$T_c = 208\text{ }^{\circ}\text{C}$		
Time interval (min)	$T_{II}$ ( $^{\circ}\text{C}$ )	$\Delta H_{fII}$ ( $\text{J g}^{-1}$ )	Time interval (min)	$T_1$ ( $^{\circ}\text{C}$ )	$\Delta H_{fI}$ ( $\text{J g}^{-1}$ )	$T_{II}$ ( $^{\circ}\text{C}$ )	$\Delta H_{fII}$ ( $\text{J g}^{-1}$ )	Time interval (min)	$T_1$ ( $^{\circ}\text{C}$ )	$\Delta H_{fI}$ ( $\text{J g}^{-1}$ )
0.5	225.7	35.6	2.5	216.7	4.6	226.4	12.1	10.0	222.4	6.3
0.6	226.4	36.6	3.2	216.7	7.3	226.4	18.3	12.5	222.7	13.3
0.7	226.4	46.6	4.5	217.1	11.1	226.7	25.3	17.0	222.7	21.4
0.8	227.1	48.9	5.5	217.1	13.4	227.1	29.5	22.0	223.1	35.6
1.0	227.1	52.6	7.0	217.1	15.5	227.1	33.2	—	—	—

Table 3

Variation of low-melting peak temperature  $T_I$ , middle-melting peak temperature  $T_{II}$ , high-melting peak temperature  $T_{III}$ , and enthalpy of fusion  $\Delta H_f$  for PTT measured at crystallization temperatures  $T_c$  of 182, 198, and 208 °C for various heating rates

$T_c = 182\text{ }^\circ\text{C}$				$T_c = 198\text{ }^\circ\text{C}$				$T_c = 208\text{ }^\circ\text{C}$		
Heat Rate (°C min <sup>-1</sup> )	$T_{II}$ (°C)	$T_{III}$ (°C)	$\Delta H_f$ (J g <sup>-1</sup> )	$T_I$ (°C)	$\Delta H_{fI}$ (J g <sup>-1</sup> )	$T_{II}$ (°C)	$\Delta H_{fII}$ (J g <sup>-1</sup> )	$T_I$ (°C)	$T_{II}$ (°C)	$\Delta H_f$ (J g <sup>-1</sup> )
5	221.4	228.6	57.9	215.9	4.9	226.9	44.2	221.6	229.0	50.5
10	221.1	227.5	56.3	216.2	7.6	226.5	41.0	222.2	227.8	59.9
20	—	226.7	52.9	217.1	15.1	226.1	31.6	223.1	—	56.1

To account for the effect of heating rate on the multiple melting behavior of PTT, separate qualitative experiments were carried out. In these experiments, each sample was isothermally crystallized at 182, 198, or 208 °C, and then its melting thermogram was recorded using three different scanning rates ranging from 5 to 20 °C min<sup>-1</sup>. Quantitative description of all the melting endotherms observed are summarized in Table 3 and, due to space limitation, only the results obtained for  $T_c$  of 208 °C are shown graphically in Fig. 5. Apparently, the positions of peaks II and III slightly decreased with increasing heating rate for the  $T_c$  of 182 °C, while that of peak I slightly increased and that of peak II slightly decreased with increasing heating rate for the  $T_c$ 's of 198 and 208 °C. The cause for the increase in the observed value of peak I may be as simple as a superheating effect, while that for the decrease in the observed values of peaks II and III should base on a more theoretical grounds. With increasing scanning rate during a heating scan, less time was available for molecules to translate onto the growth front of the recrystallizing crystallites. As a result, the recrystallized crystallites formed at a high scanning rate should be less stable than those formed at a lower scanning rate, hence the lower value of the observed peak II.

Based on the data shown in Table 3, it is obvious that, for samples crystallized at 198 °C, the weight of peak I increased, while that of peak II decreased, with increasing heating rate, and that, for samples crystallized at 208 °C, peak II was clearly visible in the thermogram recorded at 5 °C min<sup>-1</sup> and was disappeared altogether in the thermogram recorded at 20 °C min<sup>-1</sup> (see Fig. 5). The observation suggests that, during a heating scan, the less stable fraction of the primary crystallites melts (in addition to the melting of the secondary crystallites) and recrystallizes and, upon further heating, the recrystallized crystallites melts again, giving rise to the formation of peak II and, according to the evidence shown in Fig. 5, the melting of the recrystallized crystallites from melted primary crystallites during a heating scan should be largely responsible for the occurrence of peak II. Additionally, the shifting in the partial weights of peaks I and II with heating rate can be explained based on the fact that the extent of recrystallization process depends significantly on the scanning rate used. The higher the heating rate used, the shorter the time being available for the diffusion of the molecular segments onto the growing crystallites.

### 3.4. Determination of the equilibrium melting temperature

It has been shown previously that peak I corresponded to the melting of the primary crystals formed at a specified  $T_c$ ; thus, the  $T_I$  values listed in Table 1 are simply the  $T_m$  values of the crystalline aggregates formed in the samples after crystallization at the  $T_c$ . According to a theory derived by Hoffman and Weeks [43], the equilibrium melting temperature  $T_m^0$  of a semicrystalline polymer can be estimated by a linear extrapolation of the observed  $T_m - T_c$  data to the line  $T_m = T_c$ . Mathematically, they arrived at the following equation, the linear Hoffman–Weeks extrapolation (LHW):

$$T_m = \frac{T_c}{2\beta} + T_m^0 \left[ 1 - \frac{1}{2\beta} \right], \quad (2)$$

where  $\beta$  is the thickening ratio. In other words,  $\beta$  indicates the ratio of the thickness of the mature crystal  $l_c$  to that of the initial one  $l_c^*$ ; therefore,  $\beta = l_c/l_c^*$ , which is supposed to always be greater than or equal to one. The

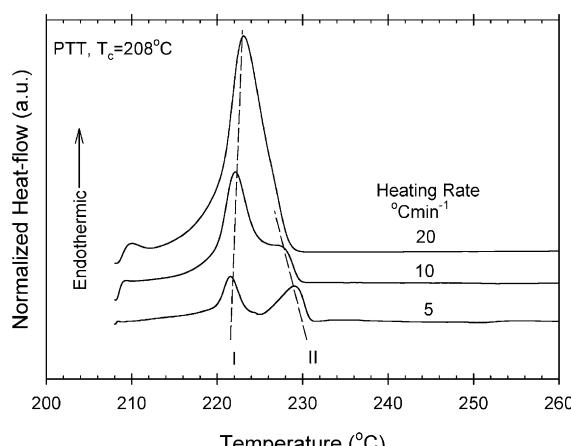


Fig. 5. Subsequent melting endotherms for PTT samples recorded using different heating rates ranging from 5 to 20 °C min<sup>-1</sup> after complete crystallization at 208 °C.

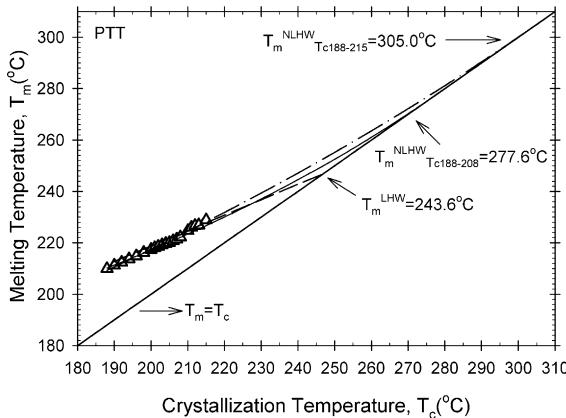


Fig. 6. Observed melting temperature of the primary crystallites as a function of crystallization temperature for PTT shown along with the linear Hoffman–Weeks extrapolation (solid line) and the non-linear Hoffman–Weeks extrapolation (dotted line, calculated using  $\beta^m = 1.00$  and  $a = 1.02$ ; dashed dot line, calculated using  $\beta^m = 1.00$  and  $a = 0.58$ ).

factor 2 in Eq. (2) suggests that the thickness of the crystals undergoing melting is approximately double that of the initial critical thickness [44].

Fig. 6 shows the plot of  $T_l$  (i.e., the observed  $T_m$  value of the primary crystallites formed at a  $T_c$ ) as a function of the  $T_c$ . It is evident that, within the  $T_c$  range of 188–208 °C, the  $T_l$  values exhibited a linear relationship with the  $T_c$ , while, within the  $T_c$  range of 210–215 °C, a deviation from the linear trend was observed. Due to the significant non-linearity of the data within the  $T_c$  range of 210–215 °C, only the  $T_l$  values collected for the  $T_c$ 's ranging from 188 to 208 °C should be used to determine the  $T_m^0$  value based on the LHW extrapolation. The LHW extrapolation on the  $T_m$ – $T_c$  data collected within the  $T_c$  range of 188–208 °C provided the  $T_m^0$  value of  $\approx 243.6$  °C, with the  $\beta$  parameter being 0.83. The value of  $\beta$  near one guaranteed (based on the assumptions of the Hoffman–Weeks derivation) that the extrapolation was valid and gave a reliable  $T_m^0$  value, because the  $T_m$  values observed for different  $T_c$  values were not greatly affected by the lamellar thickening process, which was in a good agreement with our results discussed previously.

Even though, for the  $T_m$ – $T_c$  data collected within the  $T_c$  range of 188–208 °C, the correlation coefficient  $r^2$  of the LHW fit was very close to one (i.e.,  $r^2 = 0.9989$ ), a slightly upward curvature of the data was clearly discernable. The upward curvature was more aggravated for the  $T_m$  data collected at the  $T_c$ 's greater than 208 °C. Table 4 summarizes the  $T_m^0$  values estimated from the  $T_m$ – $T_c$  data collected within different  $T_c$  ranges. Evidently, the  $T_m^0$  value based on the LHW extrapolation was found to increase from  $\approx 243.6$  to 256.0 °C, with increasing number of data point collected at  $T_c$ 's greater than 208 °C. The  $T_m^0$  values estimated in this work were

Table 4

Variation of estimated equilibrium melting temperature  $T_m^0$  according to linear Hoffman–Weeks extrapolative method for different observed melting temperature  $T_m$ , crystallization temperature  $T_c$  data ranges

$T_m - T_c$ (°C)	$\beta$	$T_m^{0\text{LHW}}$ (°C)	$r^2$
188–208	0.829	243.6	0.9989
188–210	0.802	246.1	0.9931
188–211	0.773	249.4	0.9866
188–212	0.752	252.1	0.9843
188–213	0.743	253.6	0.9855
188–215	0.728	256.0	0.9855

in the similar range to the values reported in the literature [33,34,37,38].

This upward curvature in the observed  $T_m$ – $T_c$  data was also reported for various other polymer systems [44,45], thus raising a concern on the assumed constancy of the  $\beta$  parameter. In fact, Weeks [46] pointed out long ago that the increase in the observed  $T_m$  value with increasing crystallization time may be a result of the lamellar thickening, which has a logarithmic dependence on time. This simply means that the thickening effect is much more severe at higher  $T_c$  values (as a result of a combination of high molecular mobility and a small relaxation time) where prolonged crystallization time is needed for complete crystallization.

Although the non-linearity in the observed  $T_m$ – $T_c$  data over a wide range of temperatures was explained to some extent by Alamo et al. [44], it is the recent contribution by Marand et al. [47] that offers a new method for determining the  $T_m^0$  value based on the observed  $T_m$ – $T_c$  data (provided that the  $T_m$  data obtained are essentially free from the thickening effect). Based on the Gibbs–Thomson equation (see Eq. (1)) and the proposition of Lauritzen and Passaglia [48] on the stem length fluctuation during chain folding, Marand et al. [47] proposed a new mathematical derivation that states a relationship between the observed  $T_m$  and the corresponding  $T_c$ . This equation is called the non-linear Hoffman–Weeks extrapolation (NLHW), which is written in the form:

$$\frac{T_m^0}{T_m^0 - T_m} = \beta^m \frac{\sigma_e^1}{\sigma_e^{\text{GT}}} \left[ \frac{T_m^0}{T_m^0 - T_c} + \frac{D_2 \Delta H_f^0}{2\sigma_e^1} \right], \quad (3)$$

or in a simpler form:

$$M = \beta^m \frac{\sigma_e^1}{\sigma_e^{\text{GT}}} (X + a), \quad (4)$$

where  $\beta^m$  is the thickening coefficient (equivalent to the  $\beta$  parameter),  $\sigma_e^{\text{GT}}$  is the fold surface free energy associated with a nucleus of critical size including the extra lateral surface energy due to fold protrusion and the mixing entropy associated with stems of different lengths ( $\sigma_e^{\text{GT}}$  is

the basal interfacial energy as appeared in the Gibbs–Thomson equation),  $\sigma_e^l$  is the interfacial energy associated with the basal plane of the mature crystallite,  $D_2$  is a constant, and all other parameters are the same as previously defined. It is worth noting that, for most cases, it is safe to assume that  $\sigma_e^l = \sigma_e^{GT}$  [47].

In order to apply Eq. (3) to analyze the experimental  $T_m - T_c$  data in real polymer systems, it is required that the observed  $T_m$  data be collected from samples crystallized at different temperatures but having the same lamellar thickening coefficient  $\beta^m$ . For each set of the observed  $T_m - T_c$  data, corresponding values of  $M$  and  $X$  appearing in Eq. (3) can be calculated for a given choice of the seeded  $T_m^0$  value. In the case where  $\sigma_e^l = \sigma_e^{GT}$  the “actual” equilibrium melting temperature  $T_m^0$  is taken as the seeded  $T_m^0$  value which results in the plot of  $M$  versus  $X$  being a straight line with the slope of unity (i.e.  $\beta^m = 1$ ) and the intercept of  $a$  (i.e.  $a = D_2\Delta H_f^0/2\sigma_e^l$ ).

Because it has been shown previously that lamellar thickening did not occur in PTT during crystallization, at least within the  $T_c$  range studied, it is reasonable to assume that the observed  $T_m$  data summarized in Table 1 were collected from lamellae having the same  $\beta^m$ , thus making them eligible to be analyzed according to the NLHW method. Fig. 7 shows variation of the  $M$  versus  $X$ , which was calculated from the data shown in Table 1 for different choices of the seeded  $T_m^0$  value (only the  $T_m - T_c$  data collected within the  $T_c$  range of 188–208 °C were included in this figure). Based on the virtue of this method, the  $T_m^0$  value for this PTT resin was found to be ≈277.6 °C ( $r^2 = 0.9980$ ). The value of  $a$  associated with the resulting  $T_m^0$  value was found to be ≈1.02. If all of the  $T_m$  data collected over the  $T_c$  range of 188–215 °C were included in the extrapolation, the  $T_m^0$  value according to

the NLHW extrapolation was instead found to be ≈305.0 °C ( $r^2 = 0.9877$ ), and the value of  $a$  associated with this resulting  $T_m^0$  value was ≈0.58. It should be noted that the estimated  $T_m^0$  value of 277.6 °C agreed extremely well with the value of 273 °C reported by Wu and Woo [34].

#### 4. Conclusions

Subsequent melting thermograms of PTT after isothermal crystallization at various  $T_c$  values exhibited triple (for  $T_c$ 's lower than ≈192 °C), double (for  $T_c$ 's greater than ≈192 °C but lower than ≈210 °C), or single (for  $T_c$ 's greater than ≈210 °C) endothermic melting phenomenon. These endothermic peaks were labeled as I, II, and III for low-, middle-, and high-temperature melting endotherms, respectively. For the triple melting phenomenon, it was postulated that the occurrence of peak I was a result of the melting of the primary crystallites formed at the  $T_c$ , peak II was a result of the melting of the recrystallized crystallites, and peak III was a result of the melting of the recrystallized crystallites of different stabilities. The formation of the recrystallized crystallites was postulated to be a result of the recrystallization of the crystallizable materials after the melting of the secondary crystallites and the partial melting of the less stable fractions of the primary crystallites formed at the  $T_c$ . The existence of peaks II and III was found to depend strongly on the stability of the secondary and the primary crystallites formed and on the scanning rate used during a heating scan. WAXD patterns confirmed that, within the  $T_c$  range of interest, PTT crystallized in a triclinic unit cell and changes in the  $T_c$  did not affect the crystal modification.

Lastly, the analysis of the observed  $T_m$  of the primary crystallites and the corresponding  $T_c$ , based on the linear and non-linear Hoffman–Weeks extrapolative methods, gave the estimated  $T_m^0$  values for this PTT resin of ≈243.6 and 277.6 °C, respectively.

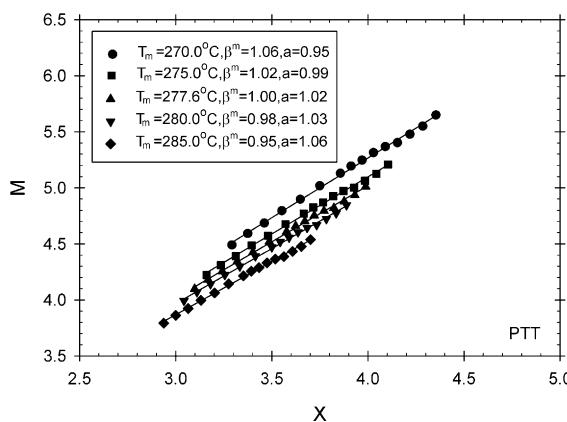


Fig. 7. Plots of the scaled observed melting temperature [ $M = T_m^0/(T_m^0 - T_m)$ ] versus the scaled crystallization temperature [ $X = T_m^0/(T_m^0 - T_c)$ ] for various choices of the seeded equilibrium melting temperature ( $T_m^0$ ) for PTT (for the data collected over the  $T_c$  range of 188–208 °C).

#### Acknowledgements

The authors wish to thank Dr. Hoe H. Chuah of Shell Chemical Company (USA), Ltd. for supply of PTT and for carrying out molecular weight measurement of the supplied resin. P. Supaphol acknowledges a grant provided by Chulalongkorn University through the Development Grants for New Faculty/Researchers. Partial support from the Petroleum and Petrochemical Technology Consortium and the Petroleum and Petrochemical College is also greatly acknowledged.

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