CHAPTER VII
CONCLUSIONS

7.1 Non-isothermal Melt-crystallization Kinetics of Poly(trimethylene terephthalate)

The non-isothermal melt-crystallization kinetic and the subsequent melting behavior of PTT for eight different cooling rates were investigated. The non-isothermal melt-crystallization exotherms of PTT showed that the temperature at 1% relative crystallinity, the temperature at the maximum crystallization rate, and the temperature at 99% relative crystallinity were all shifted towards lower temperatures with an increase in the cooling rate investigated, indicating that PTT took a shorter time to crystallize as cooling rate increased. Further analysis of the non-isothermal melt-crystallization behavior revealed that the apparent incubation period, the crystallization time at different relative crystallinity values, and the apparent total crystallization period were all found to decrease with increasing cooling rate. Interestingly, both the crystallization time at different relative crystallinity values and the apparent total crystallization period showed a linear relationship with the cooling rate in the log-log plots, with all the plots exhibiting a regression line of similar slope (i.e. the average value being ca. -0.725 $min^2 \cdot {}^oC^{-1}$). The subsequent melting behavior of PTT (recorded with a heating rate 10^oC min^{-1}) after non-isothermal melt-crystallization in DSC at eight different cooling rates showed that the melting of PTT exhibited triple melting endotherms when it was crystallized at low cooling rates (i.e. $\leq 20^oC \cdot min^{-1}$), while it showed double melting endotherms when it was crystallized at high cooling rates (i.e. $> 20^oC \cdot min^{-1}$).

The Avrami and the Tobin models were all found to describe the non-isothermal melt-crystallization data of PTT fairly well, with the Avrami model being the better of the two. The average values of the Avrami and the Tobin exponents are ca. 4.6 and 7.0, respectively. Both the Avrami and Tobin crystallization rate constants were found to increase with increasing cooling rate. The Ozawa model was also found to describe the non-isothermal melt-crystallization data of PTT fairly

well. The Ozawa exponent was found to be a slight increasing function, while the Ozawa crystallization rate constant was found to be a decreasing function, with the temperature. The ability for PTT to crystallize from the molten state under a unit cooling rate was evaluated based on the Ziabicki's kinetic crystallizability, from which it was found to be 0.98. Lastly, the effective energy barrier governing the non-isothermal melt-crystallization of PTT was found to increase monotonically with increasing relative crystallinity value.

7.2 Non-isothermal Cold-crystallization Kinetics of Poly(trimethylene terephthalate)

In this work, DSC was used to investigate the overall crystallization kinetics of PTT under nonisothermal cold crystallization condition. The Avrami, Tobin, Ozawa equation were applied to describe the nonisothermal cold crystallization kinetics. The crystallization exotherms shift to the higher temperature as the heating rate increases. The half-time of crystallization was found to decrease with increasing heating rate, suggesting that PTT take a shorter time to crystallize as the heating rate increases. From trying plot between natural logarithmic of time at various conversions and natural logarithmic of heating rate, it was found that the slope of each line is almost constant and the average value of slope is about –0.8522 and the reciprocal unit of the slope is $^{o}C\ min^{-2}$.

The average value Avrami exponent n_a is about 5.36, while the average value Tobin exponent n_t is about 7.65. Both Avrami and Tobin models provide a reasonably good fit to the experimental data for the relative crystallinity as a function of time $\theta(t)$ in the range of 0.2-0.8. For the lower relative crystallinity range [ca. $\theta(t) \leq 0.2$], the Avrami model seem to provide a better fit to the experimental data than the Tobin model. For the higher relative crystallinity range [ca. $\theta(t) \geq 0.8$], the Tobin model give a good fit more than the Avrami model. The Tobin model seems to give a fair fit to the experimental data at higher heating rates. The value of Ozawa exponent n_o lies within the range 3.63-4.90. Both K_a and K_t (i.e. crystallization rate parameter) were found to increase as heating rate increased. The Ozawa crystallization rate constant was found to increase with increasing temperature (with

the temperature range of interest), suggesting that PTT crystallizes faster with an increase in temperature.

The average value of the Ziabicki's kinetics crystallizabity of PTT crystallized from amorphous state is about 0.89. The effective energy barrier of nonisothermally cold crystallized PTT found to roughly decrease with increasing the relative crystallinity.

7.3 Miscibility, Melting, Crystallization Kinetics Behaviors, and Morphologies of PTT/PEN Blends

In this study, the miscibility, melting, crystallization behaviors, and morphologies of PTT blends have been investigated. From DSC measurement, PTT/PEN blends are miscible in amorphous state for composition range studied based on single T_g of these blends. The T_g and T_{cc} (cold-crystallization temperature) rises monotonically with increasing PEN content in the blends. The relationship between T_g and composition in these blends can be fitted well by the Gordon-Taylor equation.

The subsequent melting endotherms for PTT/PEN blends exhibited either triple (at T_c lower than 195°C for PTT and 97PTT/3PEN; at T_c lower than 192.5 for 94PTT/6PEN and 91PTT/9PEN) or double melting phenomena (at T_c greater than 195°C for PTT and 97PTT/3PEN; at T_c greater than 192.5 for 94PTT/6PEN and 91PTT/9PEN). These peaks were denoted peaks I, II, and III for low-, middle-, and high-temperature melting endotherm, respectively. For 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. The endothermic peaks I of the blends, corresponded primary melting at a various T_c, was used to determine T_m^o. Both LHW and NLHW shows that T_m^o decreases with increasing PEN content.

All of the overall crystallization rate parameters (i.e., $t_{0.5}^{-1}$, K_a, C_1, and K_{us}) were found to be very sensitive to changes in the crystallization temperature. Within

the crystallization temperature range studied (i.e., 190 < T_c < 205 °C), the values of the rate parameters for these blends were all found to increase with decreasing crystallization temperature (or with increasing degree of undercooling), suggesting that these blends crystallized at low temperatures faster than that at high temperatures. Considering at the same Tc, the $t_{0.5}^{-1}$, Ka, C1, and Kus values of 97PTT/3PEN are greater than those of pure PTT. As the content of PEN was further increased to 6 and 9 % wt, these values dramatically decreased. In addition, considering a same degree of undercooling, 91PTT/9PEN exhibited the highest values of the $t_{0.5}^{-1}$, K_a, C_1, and K_{us} followed by that of 94PTT/6PEN, 97PTT/3PEN, and PTT, respectively. The results clearly that 91PTT/9PEN crystallized the fastest, followed 94PTT/6PEN, 97PTT/3PEN, and PTT, respectively.

From PLM measurement, linear growth rate of PTT/PEN blends were measured in the temperature range 185-210°C for melt-press film. The spherulite growth rate G of PTT/PEN blends decreased dramatically as the crystallization temperature T_c is increased. When PTT/PEN blends were considered at the same T_c in ranging from 190 to 202.5°C, the growth rate of 97PTT/3PEN was greater than that of pure PTT. As the content of PEN was further increased to 6 and 9 % wt, the growth rate G dramatically decreased. For a same undercooling, the spherulite growth rate of 97PTT/3PEN is higher than that of pure PTT. For the blends with PEN content ranging from 3 to 9 % wt, the data points are interpolated by the same curve, indicating that, for a same undercooling, spherulite growth rates in the blends are unaffected by composition in range studied. Using $U^* = 1500$ cal mol^{-1} together with determine T_g and T_m^o, the kinetic parameters G_o, K_g, σ, σ_e, $\bar{q}$ was determined. PTT and 91PTT/9PEN showed the transition temperatures between regime III and II about 194°C while those of 97PTT/3PEN and 94PTT/6PEN could not observed from this crystallization temperature T_c range studied. However, the regime growth of 97PTT/3PEN and 94PTT/6PEN was found to be regime II for crystallization temperature range studied.

Banded spherulites of PTT/PEN blends were observed at crystallization temperature ranging from 185 to 202.5°C for PTT; from 185 to 200°C for 97PTT/3PEN and 94PTT/6PEN; from 185 to 197.5°C for 91PTT/9PEN. The

spacing of bands of PTT increases with increasing T_c. The spherulite texture becomes finer as T_c is decreased. The body of spherulite texture is more open with increasing PEN content. In addition, the boundary of spherulite is also changed with composition.