



## CHAPTER II LITERATURE SURVEY

### 2.1 Introduction to Poly(trimethylene terephthalate)

Poly(trimethylene terephthalate) (PTT) is a linear aromatic polyester that was first synthesized by Whinfield and Dickson in 1941 (Chuah, 2002). But it was not commercial produced because of high cost of 1,3-propanediol, one of its raw materials that used to produce PTT. PTT was recently introduced as a commercial polymer, joining the other aromatic polyesters, poly(ethylene terephthalate) (PET) and poly(buthylene terephthalate) (PBT). Commercialization of PTT was made by viable by a breakthrough in synthesis of 1,3-propanediol, which enabled the polymer to be produced at costs suitable for commercialization.

PTT has three methylene units in its chemical structure leads to higher flexibility and faster crystallization than that of PET chain. PTT is a fast crystallizing linear aromatic polyester with a melting temperature around 228°C and a glass transition temperature of 44°C (Huang and Chang, 2000). Like PET and PBT, PTT crystallizes into triclinic crystal structure. PTT c-axis chain contains two repeating units, and the methylene groups are arranged in a highly contracted gauche-gauche conformation (Chuah, 2001). Each cell contains two monomers of one polymer chain. The molecular configuration consists of rigid planar terephthaloyl residues alternating with a more flexible trimethylene sequence. The -O-CH<sub>2</sub>CH<sub>2</sub>-O- segment of the chain has a tran-gauche-gauche-trans conformation (Wu *et al.*, 2001). Isothermal crystallization studied by WAXD, found that the crystal unit cell of PTT does not change with crystallization temperature (Chung Yeh and Hong, 2002).

PTT has properties immediately between those of PET and PBT with an unusual combination of the outstanding properties of PET and processing characteristics of PBT. These characteristics made PTT highly suitable for fibers, films and engineering thermoplastics market.

Recently, Chuah (2001) studied the crystallization kinetics of PTT based on Avrami theory. He found that PTT has crystallization rate between those of PET and

and PBT when compared at the same degree of undercooling. PBT has the highest crystallization rate with Avrami rate constant ( $k_a$ ) in the order of  $10^{-2}$  to  $10^{-1} \text{ min}^{-n}$ . It is about an order of magnitude faster than PET with  $K$  of  $10^{-4}$  to  $10^{-2} \text{ min}^{-n}$ , which in turn is an order of magnitude faster than PET with  $K$  of  $10^{-4}$  to  $10^{-2} \text{ min}^{-n}$ . The same result was also reported by Huang and Chang (2000)

## 2.2 Multiple Melting Behavior in Polymer

Multiple melting is not an exclusive phenomenon for PTT. In fact, various investigators reported similar observations on a number of semicrystalline polymers, including some flexible polymers such as syndiotactic polypropylene (s-PP) (Supaphol, 2001). In syndiotactic polypropylene (s-PP), triple melting endotherms were also observed in samples crystallized at “low” temperature. The minor endotherm, located closed to the corresponding crystallization temperature, was postulated to be the melting of the secondary crystallites formed at  $T_c$ . The low-temperature melting peak was found to be the melting of the primary crystallites formed, 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 subsequent melting endotherms of s-PP was therefore described 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. Chung *et al.* (2002) and Wu and Woo (2002,2003) also reported the triple melting phenomenon similar to what has been found in this work. Chung *et al.* (2002), however, attributed the occurrence of peak I to the recrystallization during the re-heating process and peak II and III to the melting of the primary crystallites of two populations of lamellar stacks while Wu and Woo (2002) attributed the occurrence of peak I to the melting of primary crystallites. Wu and Woo (2003) also suggested that the multiple melting peaks of PTT correlated with the ringed spherulites formed at different crystallization temperatures. The rings formed cause of multiple lamellae in spherulites leading to

multiple melting peak of PTT and at condition which rings was not formed shown only single melting peak of PTT.

In addition, Many researchers reported the values of the equilibrium melting temperature  $T_m^\circ$  using linear Hoffmann–Weeks extrapolation (LHW) to be ca. 248 (Huang and Chang, 2000), 252 (Chung *et al.*, 2002), and 245.2°C (Wu and Woo, 2002). Recently, Marand *et al.* [34] proposed non-linear Hoffmann–Weeks extrapolation (NLHW) because LHW extrapolation gave an underestimated  $T_m^\circ$  in the observed  $T_m - T_c$  data over a wide range of the temperature (non-linearity of the data). The equilibrium melting temperature  $T_m^\circ$  using NLHW extrapolation (LHW) was also reported to be ca. 272.5°C (Wu and Woo, 2002).

## 2.3 Crystallization Study

### 2.3.1 Quiescent Crystallization

Supapol (2001) studied about application of the Avrami, Tobin, Malkin and Urbanovici–Segal model macrokinetic models to isothermal crystallization of syndiotactic polypropylene in quiescent state. The results suggested that the experimental data of s-PP could be best described by the Urbanovici–Segal model, followed by the Avrami, Malkin and Tobin models, respectively. A non-linear multi-variable regression program was used to fit the isothermal crystallization obtained from DSC to four kinetic equations.

Supaphol and Lin (2001) also studied crystalline memory effect in isothermal crystallization in s-PP by focusing on effect of fusion temperature. They found that on partial melting the DSC experiment suggested that the choice of the fusion temperatures used to melt the samples played an important role in determining the overall rate of isothermal crystallization, in which all the crystallization rate parameter studied were found to decrease monotonically with an increase in the value of fusion temperature up to the critical value, at which point the values of all the rate parameters approached a constant value. In contrast, they had no effect on the resulting values of the apparent crystallinity content, the long period, the lamellar thickness, and the low-melting peak temperature.

### 2.3.2 Uniaxial Stress-induced Crystallization

Yan *et al.* (2000) studied the drawing behavior of s-PS in the temperature range around its glass transition. Amorphous sheets had been prepared by quenching, and drawn at temperatures from 90-120 °C. The effect of draw ratio, draw rate and draw temperature on orientation and crystallinity were examined. They found that both orientation and crystallinity increase with increasing draw ratio and draw rate but decrease with increasing draw temperature in the temperature range of 90-114 °C. Results showed that crystallization of s-PS was predominantly controlled by stress rather than by temperature during drawing in this temperature range.

Sura Desai and Abhiraman (2001) reported that in some processes such as melt spinning, the crystallization behavior of s-PP was found substantially different from that of most other linear polymers. The anisotropic stress field in such processes led to extension as well as alignment (orientation) of the chains in the melt, both of which contributed usually to dramatic enhancement in the rate of crystallization. However, since the primary structure of s-PP chain in its most preferred crystal form was comprised of a 'coiled helical'  $-(T_2G_2)_2-$  sequence, stress-induced chain extension could lead to conformational sequences that were not favorable for crystallization in this form. As a consequence, process conditions that generated higher stress levels could cause a diminution in the rate of crystallization of this polymer.

### 2.3.3 Shear-induced Crystallization

Wolkowicz (1983) studied the effect of shear on the melt crystallization behavior of poly (1-butene) at several shear rates and degree of under cooling. Crystallization was carried out using a parallel plate rotary shearing apparatus on the stage of an optical microscope. Photograph techniques were used to record nuclei formation and size during crystallization over any shear rate. The data was analyzed in light of classical nucleation theories and Avrami kinetics. The process was characterized by a reduction of induction times and shear stress of the crystallinity melt were found to increase rapidly with the onset of crystallization.

The shear stress in the system induced a certain amount of nucleation orientation which greatly accelerated the overall crystalline transformation process. From the morphological study, he mentioned that the number of crystal particles increased exponentially with time at all shear rates and undercooling.

Ness and Liang (1993) investigated the influence of temperature and shear rate on flow behavior of HDPE melts during extrusion. A Ceast Rheovis 2100 Capillary Rheometer was used as the test apparatus in the experiments. They found that the entry pressure drop for the samples was very low during extrusion. Also, the phenomenon of shear-induced crystallization was easily produced when a die with larger entry angle was used and the temperature was near the melting point of samples, even though the shear rate was rather low.

Kim (1993) studied about memory effect of shear history of polyethylene terephthalate (PET) under shear conditions of 11.7 to 1168 s<sup>-1</sup> in a capillary rheometer. The purpose of this study was to elucidate the memory effect of shear history and to investigate the change in the crystallization kinetics of PET with different shear history by using differential scanning calorimetry (DSC) technique. The effect of shear history was reduced because of the relaxation process as the holding time in melt state before crystallization. They found that crystallization rate increase with increasing shear rate. Moreover, double peaks of heating crystallization exotherms and a low value of Avrami exponent appeared at low shear rates, which was attributed to the existence of crystallization processes with different rates. Fast process involved the disentangled molecules and the slow process involved the highly entangled molecules. For optical measurement by using optical microscope combined with hot stage it was found that the number of nuclei increased rapidly as soon as some nuclei appeared after a certain induction time but the row of nucleation could be observed in only a small fraction of samples. So the microscopic orientation was not the major sources of enhancement of crystallization rate.

Moitzi and Skalicky (1993) studied shear-induced crystallization of isotactic polypropylene melts by using special shearing equipment and synchrotron radiation. They found that if shearing rate was constant and crystallization temperature decreased, the induction time will be decreased. When crystallization temperature were fixed and shearing rate were increased and they found that

induction time also decreased. Moreover, under the same shearing conditions the entropy of the melt of material with wide molecular weight distribution was higher than that of narrow molecular weight distribution.

Kakani (1997) studied flow-induced crystallization in some semicrystalline polymers under extensional flow field. HDPE, PP and PS were used in the experiment to generate kinetic data. The crystallization rheometer was used to induce extensional flow field and the experimental data were compared to Avrami theory. He found that PS, which was a non-crystallizing material, did not show flow-induced crystallization. HDPE and PP showed similar birefringence behavior under extensional and quiescent conditions and flow-induced crystallization would be occurred after the cessation of an extensional flow-field.

Jerschow and Janeschitz-Kriegl (1997) studied about effect of long molecules in shear-induced crystallization of isotactic polypropylene by using nucleation model which was microscopic model that mentioned about highly oriented layers were based on thread-like precursors which were formed during shear flow. In this study polypropylene were sheared for a short period at 150 °C. A duct with an aspect ratio of 10/1 was used as shearing device. Near its exit two parallel glass windows were placed in the opposite large duct wall and they allowed optical measurements during and after shearing. From this experiment, it was found that the long polymer molecules had large effect for the formation of highly oriented layers due to shear treatment and polypropylene with narrow molecular mass distributions had a lower tendency to form this structure.

Churdpant and Isayev (1999) studied shear-induced crystallization in injection moldings by comparing between Ziegler-Natta and metallocene isotactic polypropylene. From rheological study found that steady shear viscosity and complex viscosity decreased as shear rate and frequency increased, respectively. The processing conditions for injection molding experiments which included inlet melt temperature, injection speed, holding time and mold temperature were varied. At the same processing condition, metallocene based i-PP showed higher thickness of skin layer, higher birefringence, higher impact strength, lower spherulite size, lower yield stress and lower degree of crystallinity than Ziegler-Natta based i-PP. For the processing conditions were found to have a little effect on mechanical properties.

Ahn Cho and Lee (2000) studied about the kinetics shear-induced crystallization in polyethylene terephthalate (PET). At low shear rate region, shear-treated samples were prepared by using controlled shear rate apparatus (CSR) and capillary rheometer was used at low shear rate region. The differences of crystallization behavior of the samples were observed using DSC. The kinetic model suggested by Hoffmann-Lauritzen and Nakamura were used to analyze experimental results. The kinetic model of shear-induced crystallization started with the concept that polymer melt with orientation reduces amount of entropy. So the orientation became easy to create nuclei thermodynamically. They found that when the shear rate increased, the crystallinity peak was shifted toward a lower temperature. The important result was the orientation of melt rapidly reached the critical amount as the shear rate increased. They also found the decrease in crystallization temperature for heating mode in non-isothermal crystallization.

Yoon *et al.* (2000) studied the effect of shearing on crystallization behavior of poly(ethylene naphthalate) (PEN) by rheological and morphological measurements. Time sweep measurements of storage modulus ( $G'$ ) and dynamic viscosity ( $\eta'$ ) were carried out on the molten PEN by Advanced Rheometric Expansion System (ARES) in the parallel plate geometry at several different temperature and frequencies, followed by structural analysis by differential scanning calorimetry, X-ray diffractometer, and polarized optical microscope. They found that the rate of isothermal crystallization of PEN notably affected by temperature, while the shear rate had an important effect on the structure of the resultant crystals and the rate of crystallization was increased with increasing shear rate at a given temperature. They also found that all diffraction peaks shifted to lower angle when frequency applied was increased. This suggest that there was deformation in the crystal structures as well.

Myung *et al.* (2001) also studied about effect of shearing on crystallization behavior of PET with a parallel-plate rheometer at different temperatures and shear rates. They found that when a constant shear rate was added to the polymeric melt, the shear stress increased with the time as a result of orientation of molecular chains. These results made the overall bulk crystallization

rate more speedy, resulting in the disappearance of the exothermic peak of PET melted at different frequencies ( $\omega$ ) when compared with zero frequency. For the effect of the time-dependent rheological parameter ( $G'$  and  $\eta'$ ) at different crystallization temperature for each frequency was found that both storage modulus and dynamic viscosity were very susceptible to structural changes and induction time was decreased with increasing temperature. This suggests that the number and growth rate of the nucleated crystallites were greater at low temperature than that at high temperature which meant that both nucleation density and growth rate of crystallites were diminished by raising the annealing temperature. From polarizing optical micrographs of PET crystallized at 240 °C confirmed that aggregation of spherulite was increased with increasing the frequency.

Watanabe *et al.* (2003) studied isothermal crystallization of polybutene-1 (PB-1) under shear flow using coaxial cylinder-type apparatus (shear flow direct observation system, SF-DOS). They introduced appropriate procedure for the elimination of overshoot in temperature profiles during cooling steps by gradually step decreasing temperature. Isothermal crystallization of PB-1 at temperature 102°C and 112°C under shear rate up to  $0.7\text{s}^{-1}$ . In this study, the band of oriented region were observed especially when the shear strain became higher and the temperature became lower, narrow bands formed after a certain time along the flow direction even at high temperature. To confirm that the bands formed were the bands of oriented structure, atactic polystyrene was used as a model of highly amorphous material. Bands similar to PB-1 were also observed at 140°C under shear flow that meant these bands should be related to the molecular orientation of polymer chains along the flow direction, but not crystallization. Moreover, they also concluded that the spherulites develop more easily in the highly oriented bands rather than in the matrix region.

Masubuchi *et al.* (2001) also studied shear induced isothermal crystallization of isotactic polypropylene (iPP) by combining DTA and SFTR. Time development of crystallinity was obtained and analyzed by the Avrami equation after subtracting the induction time. Effect of shear rate was investigated for a fixed crystallization temperature  $T_c = 142.5^\circ\text{C}$  with  $0.05\text{ s}^{-1} \leq \dot{\gamma} \leq 1.0\text{ s}^{-1}$ . To examine



effect of  $T_c$ ,  $T_c$  was varied from 138.0 to 148.0°C with fixed  $\dot{\gamma}$  of 0.2 s<sup>-1</sup>. In the range of shear rate studied, with an increase of shear rate,  $k_a$  decreased slightly and induction time,  $t_i$  decreased drastically. The increase of  $n_a$  was observed but the magnitude of the change was insignificant. The observed value of  $n_a$  suggested the spherulite growth and inhomogeneous nucleation of the crystal even under shear. It should be noted that though the experimental data can be well described by the Avrami equations, the behavior of the parameters cannot be fully understood physically. Guo and Narh (2002) proposed simplified model of stress-induced crystallization kinetics of PET under isothermal crystallization from the melt. The assumption of this model that the effect of shear stress on crystallization was only by increasing the equilibrium melting temperature  $T_m^\circ$ . The advantage of this model is that the parameters in quiescent state crystallization model do not change and can be determined easily. They found that shear stress applied not only increased the rate of crystallization, but also broadened the crystallization temperature range. The peak temperature at highest crystallization rate was also shifted to higher temperature with increasing shear stress.