



CHAPTER IV EXPERIMENTAL

4.1 Material

The PTT resins used in this study were supplied in the pellet form by Shell chemical Company (Houston, Texas, USA). Molecular characterization of PTT was carried by Dr. Chuah H.H. at Shell Chemical Company. The result showed the following molecular weight information; the weight average molecular weight (\overline{M}_w) and number average molecular weight (\overline{M}_n) were 78,132 and 34,656, respectively.

4.2 Methodology

4.2.1 Multiple Melting Behavior in Isothermally Crystallized PTT

4.2.1.1 *Sample Preparation*

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

4.2.1.2 *Differential Scanning Calorimetry Measurements*

In this experiment, a DSC (DSC-7, Perkin-Elmer) was used to follow isothermal crystallization exotherm and subsequent melting endotherm of these polyester resins. Calibration for temperature scale was carried out using pure indium standard on every other run to ensure accuracy and reliability of the data obtained. To minimize thermal lag between polymer sample

and DSC furnace, each sample holder was loaded with sample weighing around 8.0 ± 0.3 mg. It is worth noting that 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°C at a heating rate of $80^\circ\text{C}\cdot\text{min}^{-1}$ to a desired fusion temperature T_f at 260°C for a holding period of 5 min. After this period, each sample was rapidly cooled (i.e., ca. $200^\circ\text{C}\cdot\text{min}^{-1}$) from T_f to a desired crystallization temperature, 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). Both the isothermal crystallization exotherms and subsequent melting endotherms were recorded for further analysis at different heating rate.

4.2.1.3 Differential Crystal Structure and Crystallinity

Measurements

Wide-angle X-ray diffraction (WAXD) technique was employed to determine crystal modification of PTT samples prepared in the same conditions set forth for samples prepared for the DSC measurements (viz. after the samples were completely crystallized at a desired crystallization temperature, they were immediately quenched to 30°C). Each sample was then taken out of the DSC sample holder and was pasted onto a glass X-ray sample holder using vasaline as adhesive. The WAXD intensity pattern of each sample was then collected on a Rigaku Rint 2000 diffractometer, equipped with a computerized data collection and analytical tools. The X-ray source ($\text{CuK}\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$) was generated with an applied voltage of 40 kV and a filament current of 30 mA.

4.2.2 Effects of Crystalline and Orientational Memory Phenomena on Isothermal Bulk Crystallization and Subsequent Melting Behavior of PTT

4.2.2.1 Sample Preparation

Poly(trimethylene terephthalate) PTT pellets was dried in a vacuum oven at 140°C for 5 hours. A film of PTT samples each resin was melted-pressed at 260°C for PTT in a Wabash V50H compression molding machine under a pressure of $4.62 \times 10^2 \text{ MNm}^{-2}$. After 5 min holding time, the film was taken out and allowed to cool at the ambient condition down to room temperature between the two metal platens. This treatment assumed that previous thermo-mechanical history was essentially erased, and provided a standard crystalline memory condition for the as-prepared film. For sheared sample, Instron capillary rheometer model 4303 was used to apply the different shear memory. The shear rates used were 92.1, and 245.6 s^{-1} . Temperature used to shear the sample was set at 250°C. The cylinder was filled with solid resin, preheated for 10 min and molten resin which was treated with fixed shear rate was extruded out, and then quenched with liquid nitrogen. The L/D ratio and the diameter of capillary used were 40.16 and 1.25 mm, respectively. For simplicity, the as-prepared neat samples were hereafter called S0, while the as-prepared sheared samples using the wall shear rates of 92.1 and 245.6 s^{-1} were hereafter called S92.1 and S245.6, respectively.

4.2.2.2 Differential Scanning Calorimetry Measurements

In this experiment, a DSC (DSC-7, Perkin-Elmer) was used to follow isothermal crystallization and subsequent melting behavior of these polyester resins. Calibration for temperature scale was carried out using a pure indium standard on every other run to ensure accuracy and reliability of the data obtained. To minimize thermal lag between polymer sample and DSC furnace, each sample holder was loaded which weighed around $8.0 \pm 0.3 \text{ mg}$. It is worth noting that 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°C at a heating rate $80^\circ\text{C min}^{-1}$ to a desired fusion temperature T_f at 260°C for a holding period of 5 min. After this period, each sample was rapidly cooled (i.e. around $200^\circ\text{C min}^{-1}$) from T_f to a desired crystallization temperature, 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). The isothermal crystallization exotherms and the subsequent melting endotherms at a heating rate $10^{\circ}\text{Cmin}^{-1}$ for various values of isothermal crystallization temperature. The analysis of the experimental data was carried out using a non-linear multivariable regression program to directly fit the experimental data to the respective macrokinetic models.

4.2.2.3 *Crystal Structure and Crystallinity Measurements*

Wide-angle X-ray diffraction (WAXD) technique was employed to determine the crystal modification and the apparent degree of crystallinity of PTT samples prepared according to the isothermal crystallization condition set forth for the DSC measurements, followed with quenching ($200^{\circ}\text{Cmin}^{-1}$) to 30°C . Each sample was then removed from DSC sample holder and was pasted onto a glass sample holder. The WAXD intensity patterns of the sample were then collected on a Rigaku Rint 2000 diffractometer (CuK α radiation, $\lambda = 1.54 \text{ \AA}$) equipped with a computerized data collection and analytical tools. The X-ray source was operated at a voltage of 40 kV and a filament current of 30 mA.

4.3.3 Quiescent and Shear-induced Cold Crystallization in PTT

4.3.3.1 *Sample Preparation*

For zero shear rate sample, PTT pellets clear grade were dried in a vacuum oven at 140°C for 5 hours prior to further use. A film of approximately $200 \mu\text{m}$ in thickness for each resin was melted-pressed at 260°C for PTT in Wabash V50H compression molding machine under an applied pressure of $4.62 \times 10^2 \text{ MN}\cdot\text{m}^{-2}$. After 5 min holding time, the film was taken out and allowed to cool at the ambient condition down to room temperature between the two metal platens. This treatment assumes that previous thermo-mechanical history was essentially erased, and provided a standard crystalline memory condition for the as-prepared film. For low shear rate samples, PTT pellets were dried in the oven at 140°C for 5 hours. Then the pellets were put into the mold which circle geometry to compress into the disk shape samples following by shearing samples using a cone

and plate rheometer (Rheometrics Scientific, model ARES). The disk shape samples were inserted between cone and plate rheometer and heated up to a desired fusion temperature T_f at 250°C. When the sample was melted completely, the excess sample was squeezed out and held until the temperature was equilibrated. Before beginning of the test, the gap was adjusted to exact distance of 0.051 mm. When the equilibrium temperature was reached, the experiment was started in the transient mode. The shear rate used were 5 and 10 s⁻¹ with different shearing time at 1, 3, and 5 min for both shear rates. After the cessation of shear, the sample was quenched immediately in liquid nitrogen bath to freeze the molecular structure of polymer before studying crystallization behavior with DSC technique.

For high shear rate samples, PTT pellets were dried in oven at 140°C for 5 hours. before filling in the barrel of capillary rheometer. A capillary rheometer Instron model 4303 was used to applied shear stress to polymer samples before studying shear-induced crystallization with DSC technique. The diameter of die and L/D ratio are 1.25 mm and 40.15, respectively. Preheat time used was about 10 min. When the shear treated sample were extruded pass through a capillary die, they were cut and quenched immediately in liquid nitrogen bath. The shearing temperature used in this work was 250 and 260°C at various shear rates.

4.3.3.2 *Differential Calorimetry Measurements*

For In this experiment, a DSC (DSC-7, Perkin-Elmer) was used to follow isothermal crystallization and subsequent melting behavior of these polyester resins. Calibration for temperature scale was carried out using indium standard on every other run to ensure accuracy and reliability of the data obtained. To minimize thermal lag between polymer sample and DSC furnace, each sample holder was loaded which weighed around 8.0 ± 0.3 mg. It is worth noting that each sample was used only once and all the runs were carried out under nitrogen atmosphere to prevent extensive thermal degradation. To prepare quenched sample at zero shear rate, PTT film was heated from 40 to 280°C at a heating rate of 80°C·min⁻¹ to a fusion temperature T_f at 250 and 260°C for a holding period of 5 min. Then DSC pan which contained sample inside was removed as quickly as

possible from DSC sample holder and immediately immersed in liquid nitrogen bath for 10 min. The DSC pan was inserted again to DSC sample holder and heated up to 260°C with different heating rate.

For low shear rate and high shear rate samples, they were just heated from 25°C to 260°C at different heating rate. Crystallization exotherms and subsequent melting endotherms were observed with the same method as PTT sample at 0 s⁻¹ shear rate.

4.2.4 Quiescent and Shear-induced Melt Crystallization in PTT

4.2.4.1 *Sample Preparation*

For shear untreated samples, PTT pellets clear grade were dried in a vacuum oven at 140°C for 5 hours prior to further use. A film of approximately 200 μm in thickness for each resin was melted-pressed at 260°C for PTT in Wabash V50H compression molding machine under an applied pressure of $4.62 \times 10^2 \text{ MN} \cdot \text{m}^{-2}$. After 5 min holding time, the film was taken out and allowed to cool at the ambient condition down to room temperature between the two metal platens. This treatment assumes that previous thermo-mechanical history was essentially erased, and provided a standard crystalline memory condition for the as-prepared film. For disk shape samples, PTT pellets were dried in the oven at 140°C for 5 hours. Then the pellets were put into the mold with circle geometry to compress into the disk shape samples with thickness ca. 1 mm. For high shear rate samples, PTT pellets were dried in the oven at 140°C for 5 hours before filling in the barrel of capillary rheometer. A capillary rheometer (Instron model 4303) was used to applied shear stress to polymer samples before studying shear-induced crystallization. The diameter of die and L/D ratio are 1.25 mm and 40.15, respectively. Preheat time used was ca. 10 min. When the shear treated sample were extruded through a capillary die, they were cut and quenched immediately in liquid nitrogen bath. The shearing temperature T_s used were 250 and 260°C.

4.2.4.2 Methods

For rheological measurements were carried out using a cone and plate rheometer (Rheometrics Scientific, model ARES). The disk shape samples were inserted between cone and plate geometry and heated up to a desired fusion temperature at 260°C. When the sample was melted completely, it was cooled to a desired crystallization temperature. Then shear rate was applied to observe the variation of stress as function of crystallization time. A DSC (DSC-7, Perkin-Elmer) was used to follow isothermal crystallization and subsequent melting behavior of these polyester resins. Calibration for temperature scale was carried out using a indium standard ($T_m^\circ = 156.6\text{ }^\circ\text{C}$ and $\Delta H_f^\circ = 28.5\text{ Jg}^{-1}$) on every other run to ensure accuracy and reliability of the data obtained. To minimize thermal lag between polymer sample and DSC furnace, each sample holder was loaded which weighed around $8.0 \pm 0.3\text{ mg}$. It is worth noting that each sample was used only once and all the runs were carried out under nitrogen atmosphere to prevent extensive thermal degradation.

Isothermal crystallization from melt of non-sheared and sheared sample from capillary rheometer started with heating each sample from 40°C at a heating rate of $80^\circ\text{C}\cdot\text{min}^{-1}$ to a desired fusion temperature T_f at 260°C. To ensure complete melting, the sample was kept at the respective T_f for a holding period of 5 min. After this period, each sample was rapidly cooled (i.e., ca. $200^\circ\text{C}\cdot\text{min}^{-1}$) from T_f to a desired crystallization temperature, 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). Non-isothermal crystallization from melt of non-sheared and sheared sample from capillary rheometer started with heating each sample from 40°C at a heating rate of $80^\circ\text{C}\cdot\text{min}^{-1}$ to a desired fusion temperature T_f at 260°C for 5 min. Then the samples were cooled at different cooling rate to observe melt crystallization exotherms.