

## CHAPTER VIII

### CONCLUSIONS AND RECOMMENDATIONS

The overall isothermal melt-crystallization and subsequent melting behavior of six metallocene-catalyzed syndiotactic polypropylene (sPP) resins having different molecular characteristics were investigated using differential scanning calorimetry (DSC) technique. Two sets of these sPP resins were synthesized from two different catalyst systems at three different temperatures. The first set contained three resins having the weight-average molecular weight in the range of 99,000 to 188,000 Da and the racemic pentad contents in the range of ca.78 to 83%, while the second set contained three resins having the weight-average molecular weight in the range of 407,000 to 952,000 Da and the racemic pentad contents in the range of ca.79 to 88%.

The overall isothermal melt-crystallization studies revealed that the crystallization rates of these sPP resins depended on the syndiotacticity level rather than on the molecular weight, with sPP resin having higher syndiotacticity level being found to have a higher crystallization rate (for a given crystallization temperature) than that having lower syndiotacticity level. The experimental data were found to be best described by the Urbanovici–Segal model, followed by the Avrami and the Malkin ones, respectively. For a given resin, all of the overall crystallization rate parameters were found to decrease in their values with increasing the crystallization temperature, a characteristic of the crystallization in the nucleation controlled region. Comparison of the bulk crystallization rates of these resins for a given crystallization temperature suggested that the crystallization rates of these resins fell on the following order sPP#11 > sPP#14 > sPP#10 > sPP#13 > sPP#9 > sPP#12. Based on the values of the effective activation energy describing the overall isothermal melt-crystallization process estimated for these resins, the crystallization ability of these resins fell on the following sequence: sPP#11 > sPP#14 > sPP#13 > sPP#10 > sPP#9 > sPP#12.

Two extrapolative methods, namely the linear and non-linear Hoffman–Weeks, were used to estimate the equilibrium melting temperature  $T_m^0$  for each of these sPP resins. The estimated  $T_m^0$  values based on the linear Hoffman–Weeks

method were found to lie in the following order: sPP#11 > sPP#14 > sPP#10 > sPP#13 > sPP#9 > sPP#12, while those based on the non-linear Hoffman–Weeks method were in the following sequence: sPP#11 > sPP#10 > sPP#14 > sPP#13 > sPP#9 > sPP#12. In general, the estimated  $T_m^0$  values were found to increase with increasing syndiotacticity level. By plotting these values along with the values obtained from the literature as a function of the racemic pentad content, the  $T_m^0$  value for a perfect sPP was estimated to be ca. 174°C, and, based on a modified Flory's theory for the depression of the  $T_m^0$  value of a random copolymer, the  $T_m^0$  value for a perfect sPP was, instead, estimated to be ca. 167°C.

Study on non-isothermal melt-crystallization and subsequent melting behavior for these sPP resins showed that, for a given sPP resin, the crystallization exotherm became wider and shifted towards a lower temperature with an increase in the cooling rate used. Among all of the sPP resins investigated, the crystallization exotherm of sPP#11, in comparison with other sPP resins, for a given cooling rate was found to locate at the highest temperature range, followed by that of sPP#14, sPP#10, sPP#13, sPP#12, and sPP#9, respectively. The results suggested that, based on the absolute temperature scale, sPP#11 showed the highest tendency, among all of the sPP resins studied, to start crystallizing during a cooling scan. The ability for these resins to start crystallizing was found to be very similar when the difference in the equilibrium melting temperature of these resins was taken into account. The Avrami, Urbanovici–Segal, Ozawa, and Ziabicki models were found to describe the non-isothermal melt-crystallization data of these sPP resins fairly well. Lastly, the subsequent melting behavior of these sPP resins showed either a single melting endotherm or double melting endotherms. Generally, for a given sPP resin, the low-temperature melting endotherm was found to increase in its size and sharpness and move towards a higher temperature with decreasing cooling rate, while the high-temperature melting endotherm was found to get smaller with decreasing cooling rate or even disappeared altogether at some low enough cooling rates.

Non-isothermal melt-crystallization and subsequent melting behavior of neat MDPE and MDPE filled with three types of pigments (i.e. quinacridone, phthalocyanine, and diarylide) in various amounts ranging between 0.1 and 0.4 phr

were investigated using differential scanning calorimetry. For each type of sample investigated, the crystallization exotherm became wider and shifted towards a lower temperature range when the cooling rate increased. All of the pigments investigated were able to shift the crystallization exotherm towards a higher temperature range, indicating that these pigments promoted the formation of heterogeneous nuclei. Among the various pigments, phthalocyanine was the best in shifting the crystallization exotherm towards a higher temperature range, followed by quinacridone and diarylide, respectively. However, diarylide was the only pigment that was effective in accelerating the crystallization processes of the filled polymer.

Non-isothermal melt-crystallization and subsequent melting behavior of neat isotactic polypropylene (iPP) and iPP samples filled with titanium(IV)oxide ( $\text{TiO}_2$ ) nanoparticles having different surface characteristics [i.e. neat, silica ( $\text{SiO}_2$ )-coated, and stearic acid-coated] in various contents ranging from 5 to 30 wt% were investigated using differential scanning calorimetry (DSC). The cooling rate used ranged between 5 and  $30^\circ\text{C min}^{-1}$ . With increasing cooling rate, the crystallization exotherm for all of the samples investigated became larger and shifted towards a lower temperature. The crystallization peak temperature ( $T_p$ ) for all of the iPP samples filled with neat  $\text{TiO}_2$  nanoparticles were slightly greater than those of the neat iPP (by about  $1.4\text{--}3.6^\circ\text{C}$ ) and was not affected by the variation in the filler content (about  $2.3\text{--}2.6^\circ\text{C}$  on average). For iPP samples filled with stearic acid-coated  $\text{TiO}_2$  nanoparticles, the  $T_p$  values were not much different from those of the neat iPP. For iPP samples filled with 5, 20, and 30 wt%  $\text{SiO}_2$ -coated  $\text{TiO}_2$  nanoparticles, marked differences in the  $T_p$  values in comparison with those of the neat iPP were observed (about  $6.5\text{--}7.9^\circ\text{C}$  on average). Coupled with the crystallization kinetic analysis by the Avrami model, the ability for the various types of  $\text{TiO}_2$  nanoparticles to nucleate iPP matrix can be ranked as follows:  $\text{SiO}_2$ -coated  $\text{TiO}_2$  nanoparticles > neat  $\text{TiO}_2$  nanoparticles > stearic acid-coated  $\text{TiO}_2$  nanoparticles. Lastly, incorporation of the nanoparticles caused the rigidity of the resulting composites to increase (especially when the filler content was greater than or equal to 20 wt%).