Effect of Supercritical Gas on Crystallization of Linear and Branched Polypropylene Resins with Foaming Additives

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The thermal behaviors of linear and branched polypropylene (PP) with foaming additives were investigated using a normal and a high-pressure differential scanning calorimeter (DSC). Specifically, the effects of material branching, dispersed additives, cooling rates, and dissolved blowing agents on the crystallization temperature of PP resins were elucidated. Introducing branches between polymer chains increased the crystallization temperature of PP significantly. Foaming additives such as talc and glycerol monostearate (GMS) as well as processing parameters such as cooling rate also played major roles during the crystallization process. The experimental results indicate that the crystallization temperature increases up to 30 °C by introducing branches and/or adding additives to the PP materials. However, the crystallization temperature was lowered as the supercritical fluid (such as nitrogen or carbon dioxide) was dissolved in the branched PP. The effect of hydraulic pressure was identified by performing DSC study by employing helium as an inert gas, which has a very limited solubility in the polymer matrix.

Introduction

Due to its outstanding functional characteristics and low material costs, PP has been considered as a substitute for other thermoplastic materials in industrial applications. PP is a member of the semicrystalline polyolefin family, which is resistant to chemicals and abrasion. PP has a number of advantages over polystyrene and polyethylene.[1] PP has a higher rigidity as compared to other polyolefins; PP offers higher strength as compared to polyethylene and better impact strength as compared to polystyrene, and PP provides a higher service temperature range and good temperature stability as compared to other polyolefins. However, only limited research has been conducted on the production of PP foams because of their weak melt strength and melts elasticity, which makes comparison of the foam with that of other plastics difficult.[2]

In this context, long-chain branched PP materials with high melt strength have been developed as a foamable grade.[3−7] Few studies have investigated the effect of branching on the crystallization behaviors of PP resins.[8−10] It was observed that the introduction of branching in the PP resins increases crystal nuclei density. This promotes faster crystallization, and, hence, higher crystallization temperatures were observed for branched materials as compared to linear materials.

It is certain that the nucleating agent used in the foam processing plays an important role in determining the cellular structure of thermoplastic foams. The final foam structure is usually unacceptable without the addition of a nucleating agent unless a thermodynamic instability via a rapid solubility drop is utilized to promote a large number of nuclei.[11,12] In other words, if the nucleating agent is not added, the cell density becomes too low, and the bubble size becomes too large. Moreover, it has been discovered that even a small amount of nucleating agent could significantly lower the processing pressure and pressure drop rates which were required for the production of foam with a large cell density.[11,12] It is beneficial if a high nuclei density can be obtained at a lower pressure and with a smaller pressure drop rate by adding a small amount of nucleating agent/additive.

The understanding of the thermal behaviors of the polymer/additive system is critical in the processing of semicrystalline polymers as crystallization is strongly affected by the foaming additives dispersed in the polymer melt matrix. The effects of heterogeneous nucleating agents including talc and calcium carbonate on the crystallization of PP have been previously studied.[13−19]

In the extrusion foaming process, two kinds of blowing agents can be used: chemical and physical blowing agents. Chemical blowing agents can decompose at processing temperatures and produce gases necessary for foaming, while directly injected physical blowing agents can dissolve into the polymer melt in the extruder. Because the dissolved gas under high pressure in the foaming process would vary the crystallization temperature of the polymer, the effect of gas on the thermal behavior needs to be investigated. Dey et al. studied the effect of physical blowing agents on the crystallization temperature of polymer melts using a specially designed high-pressure reactor.[20] The crystallization temperature of LDPE was measured as a function of gas pressure by monitoring the sample temperature using a thermocouple attached to the lid of the reactor. A variety of techniques have been employed to investigate the thermal behavior of polymer and compressed gas systems.[21] A differential scanning

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calorimeter (DSC) was employed to scan polymer sample which was presaturated with gas. However, a loss of gas was unavoidable during the sample handling and scanning.[22] A sealed high-pressure DSC pan was also used to scan a polymer−gas system.[23] Handa et al. developed a high-pressure calorimetric technique to investigate the glass transition depression characteristics of PMMA with compressed gas.[24] They also studied the effect of supercritical CO_2 on the polymorphism in syndiotactic polystyrene[25,26] and the plasticization effects of polymers with high-pressure gases.[21,24]

He and Zoller studied the crystallization kinetics of PP, polyamide, and poly(ethylene terephthalate) (PET) using a pressure dilatometer to follow the volume changes associated with the crystallization process.[27] In addition, Zhang and Handa reported the CO_2-assisted melting of semicrystalline polymers such as polystyrene and poly(ethylene terephthalate) using a high-pressure DSC.[28] Crystallization of amorphous polymers induced by supercritical CO_2 has been investigated and compared with thermal crystallization.[22,29,30] Amorphous poly(ethylene terephthalate), poly(vinylidenefluoride)/ poly(methyl methacrylate) blends, and bisphenol A polycarbonate have been used for those studies. It can be concluded that the plasticization of CO_2 can facilitate crystallization in certain polymers to an extent comparable to that achieved using an organic liquid or vapor. Takada et al. have investigated the effect of dissolved CO_2 on the crystallization behaviors of semicrystalline polymers such as PP, poly(ethylene terephthalate) (PET), and poly (L Lactide) (PLLA).[31−33] They concluded that the dissolved CO_2 decreased the overall crystallization rate of PP within the nucleation dominated temperature region. They suggest that the dissolved CO_2 decreases the melting and the glass transition temperatures and prevents formation of critical size nuclei.[31] They also show that the presence of CO_2 in the PET increased its overall crystallization rate. CO_2 also decreased the glass transition temperature and the melting temperature of PET.[32] Finally, they indicated that CO_2 has also decreased the glass transition temperature and the melting temperature of PLLA.[33]

The crystallization behavior of semicrystalline materials is a critical factor in plastic foam processing. In a typical extrusion foaming process, the temperature of the melt decreases due to external cooling outside the foaming die and due to the cooling effect resulting from isentropic expansion of the blowing gases. Thus, the processing temperature at the final stage determines the time required for the polymer melt to solidify. For semicrystalline polymers, it was observed that the polymer melt solidifies at the moment of crystallization. Therefore, the foam structure "freezes" at the crystallization temperature which will affect the cell growth mechanism to a point where the foam cannot be fully expanded.[34,35] In addition to the effects of the processing parameters on the crystallization, the materials parameters and foaming additives can also contribute to changes in crystallization temperatures. The crystallization behaviors of linear and branched PP resins with the dispersed foaming additives and supercritical gases are investigated in this paper.

Experimental Section

Materials. Linear and branched PP materials with

degree of long chain branching of the branched PP is 0.21 per 1000 carbon atoms. They were supplied by Borealis AG Austria, and they are denoted in this paper as Linear P1 and Branched P1, respectively. Talc (A7 with a top-cut of 7 microns, Naintsch) and glycerol monostearate (GMS, Pationic 909, PATCO Polymer Additives) were used as foaming additives in this study. Helium (BOC Gas 99.9% purity), nitrogen (BOC Gas 99.9% purity), and carbon dioxide gases (BOC Gas, 99.5% purity) were used in the high-pressure experiments.

DSC Measurements. The crystallization experiments were performed with a DSC (TA Instruments, DSC 2910). In particular, a regular DSC cell and a high-pressure DSC cell were used in the experiments. The regular DSC cell was used for investigating the effects of branching, additives, and cooling rate on the crystallization behavior of the PP materials. The high-pressure DSC cell was used for investigating the effects of dissolved gases on the crystallization behavior of PP materials. The calibration was conducted using indium. The purging gas used was nitrogen at a flow rate of 50 mL/min. Samples for the DSC experiments (typical weight 3−4 mg) were taken from the extrudate in the form of a very thin disk (typical thickness 150−200 μm).[36] For the nonisothermal experiments, the samples were pressurized to 1.37, 2.75, 4.13, and 5.51 MPa and then heated to 220 °C and kept at this condition for 30 min to erase the thermal history.[37] Following this step, the samples were cooled at 10 °C/min (if not specified) to 50 °C. Next, the samples were heated at 10 °C/min up to 200 °C. During the cooling and heating processes, the crystallization and melting patterns of the samples were recorded. The degree of crystallinity was determined based on the heating cycle in the DSC thermogram. The percent crystallinity is measured as the ratio of the heat of fusion for PP materials (the area of the melting endotherm) and the heat of fusion of 100% crystalline polymers. It should be noted that efforts were made to conduct isothermal experiments for PP and PP materials with foaming agents; however, the crystallization was so quick and the shift in the exothermic heat flow curves[31,32] could not be observed. Further studies need to be conducted to verify the isothermal behavior for PP resins with foaming additives.

Results and Discussion

Experiments with the Regular DSC Cell. Effect of Branching. Figure 1 shows the cooling sections of the DSC thermograms obtained from linear and branched PP without any additives. The cooling rate was fixed to be 10 °C/min. It was observed that the branching of PP chains significantly promoted the crystallization kinetics of the PP resins by increasing the crystallization temperature about 20 °C. This result supports the findings of previous studies.[8,9] Figure 1 also illustrates that the peak of linear PP materials shows a shoulder (or double peak) in the peak caused by two-stage crystallization.[18,38,39] It can be understood that the interactive motion of the PP matrix layer at the particle surface changes the crystallization speed of the PP matrix which results in the double peaks crystallization on the DSC thermogram.[18]

Effects of Foaming Additives. The thermal behaviors of linear and branched PP resins with foaming
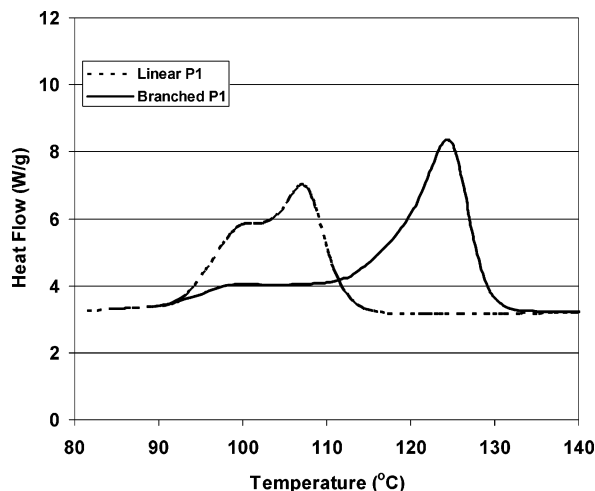
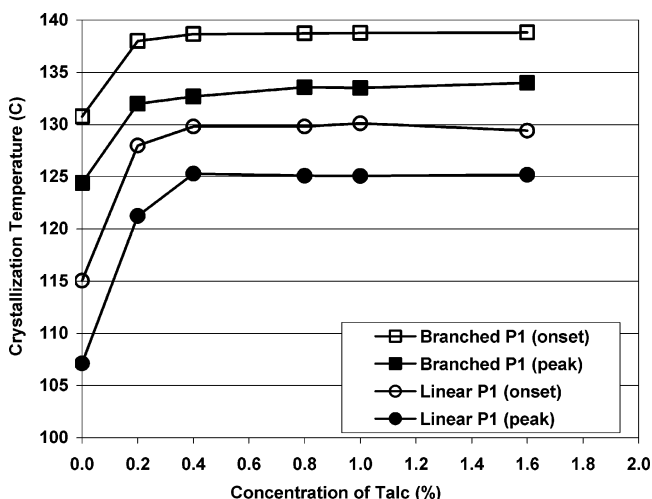**Figure 1.** DSC thermograms of linear and branched PP.

Figure 2. Effects of talc on the crystallization behaviors of linear and branched PP.

Figure 3. Effects of talc on the degree of crystallinity of linear and branched PP.

Figure 4. Effects of GMS on the crystallization behaviors of linear and branched PP.

Figure 5. Effects of GMS on the degree of crystallinity of linear and branched PP.

changed from 0 to 1.6 wt % and 0 to 1.0 wt %, respectively. The experiments were conducted at a cooling rate of 10 °C/min.

Figure 2 shows the effects of talc amounts on the crystallization temperature of PP materials. The effects of talc were more prominent in the linear PP than in the branched PP. After showing a sharp increase in the crystallization temperature as the talc concentration increased from 0 to 0.2 wt %, the crystallization temperature did not change much above 0.2 wt %. Figure 2 shows that the crystallization temperature of the branched PP is only 5−10 °C higher than that of the linear PP with a talc content ranged 0.8−1.6 wt %. It should be noted that the crystallization temperature of branched PP is 10−20 °C higher than that of linear PP without any talc particles. On the other hand, the degree of crystallinity of linear and branched PP resins was also measured, and the results are shown in Figure 3. It was observed that the degree of crystallinity of branched and linear PP increased moderately as the talc concentration increased.

Very similar results were obtained in the GMS case (Figures 4 and 5). The GMS, used as an aging modifier, also increased the crystallization temperatures and the degrees of crystallinity of linear and branched PP resins. However, because of its strong tendency of migration
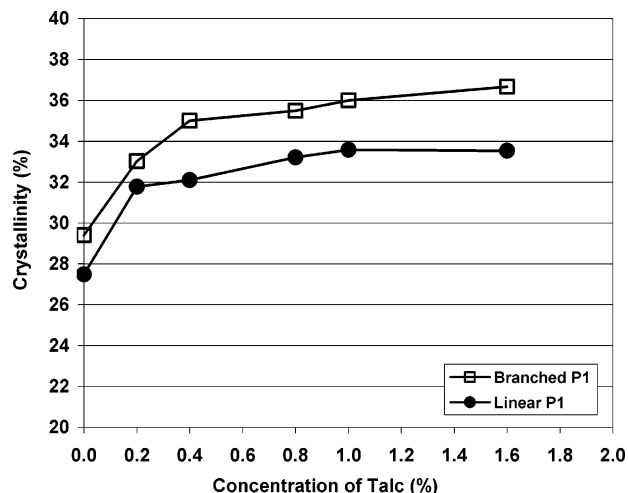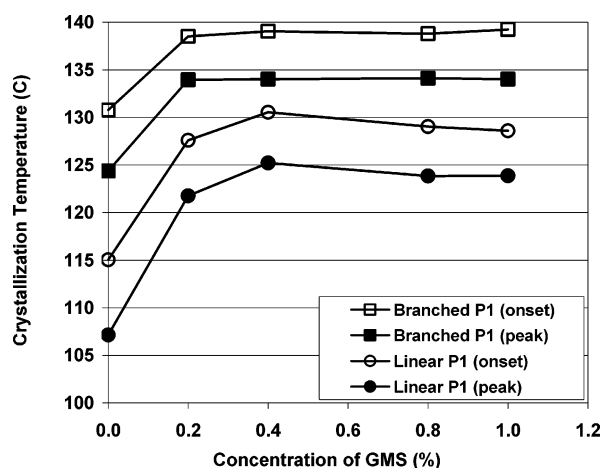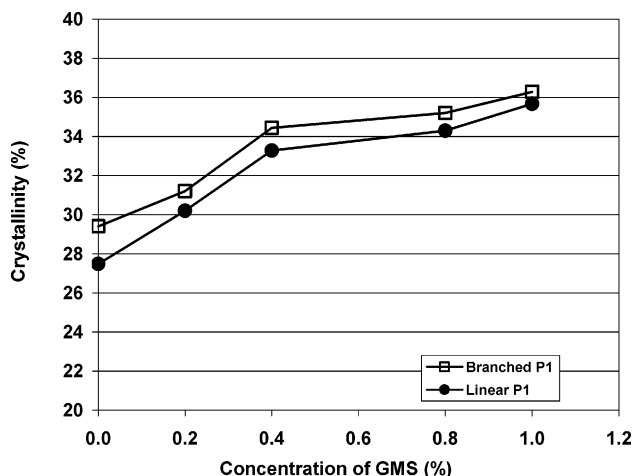
believed that the variations shown in Figure 4 are due to the nonuniform distribution of the GMS particles. The DSC sample cuts were made perpendicular to the direction of the flow from a thin filament extrudate (about 4 mm in diameter) to minimize the effect of
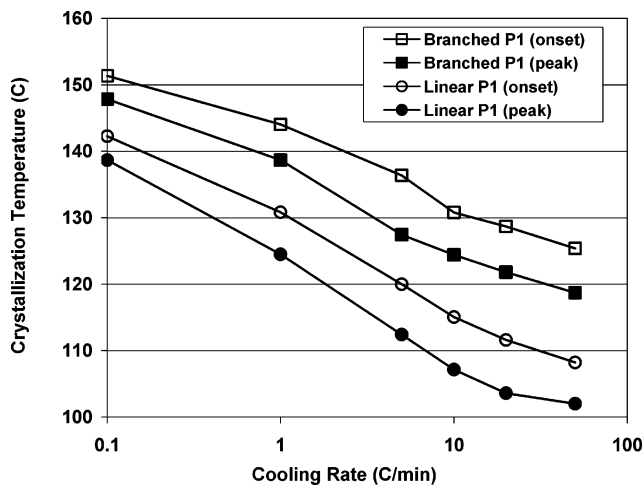
Figure 6. Effects of cooling rate on the crystallization behaviors of linear and branched PP.

Effect of Cooling Rate. The effects of cooling rate on the crystallization kinetics of linear and branched PP resins were also investigated. The cooling rate was varied from to 50 °C/min. Figure 6 shows the dependence of crystallization temperature on the cooling rate for the linear and branched PP materials. It was observed that the crystallization temperatures of PP resins were very sensitive to the change of cooling rate: the crystallization temperatures decreased by 25−30 °C as the cooling rate increased from 0.1 to 50 °C/min.

Experiments with the High-Pressure DSC Cell. Design of Cooling System for the High-Pressure DSC Cell. To investigate the effects of dissolved gas on the crystallization behavior of a polymer, a high-pressure DSC cell was used for this experiment. Due to the poor cooling capability in the pressure DSC cell, only the heating mode has been mainly used in the high-pressure experiments.

A cooling system was developed to provide the existing high-pressure cell with a cooling capability. The cooling system enables the measurements of the crystallization behavior of a polymer melt under high pressure by mounting a cooling coil connected to a liquid nitrogen dispensing unit which supplies liquid-nitrogen at a controlled rate. The design for this cooling system is shown in Figure 7. Critical experiments were conducted to verify the pressurizing and cooling functions of the modified pressure cell. The pressure was raised inside the modified high-pressure cell from atmospheric pressure to 5.51 MPa, and at this pressure a uniform cooling rate up to 30 °C/min was successfully achieved. Additionally, the crystallization behavior of the PP materials measured with the high-pressure DSC cell was compared to that of a regular cell operating at atmospheric pressure. The crystallization thermograms of PP materials were determined at atmospheric pressure using both of the DSC cells, and they were found to be nearly identical at the same cooling rates.

Finally, using this design, the measurements of crystallization kinetics under high pressure were successfully carried out using the modified high-pressure DSC cell.

Effect of Supercritical Gases. Figures 8 and 9 show the effects of pressure related to various gases on the crystallization behaviors of linear PP materials
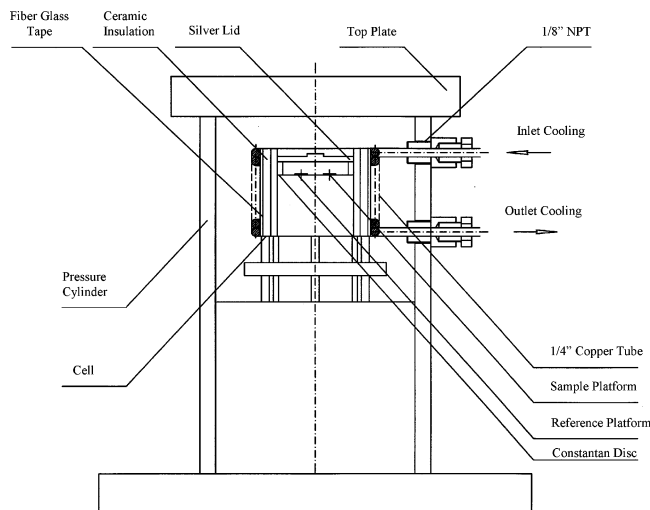

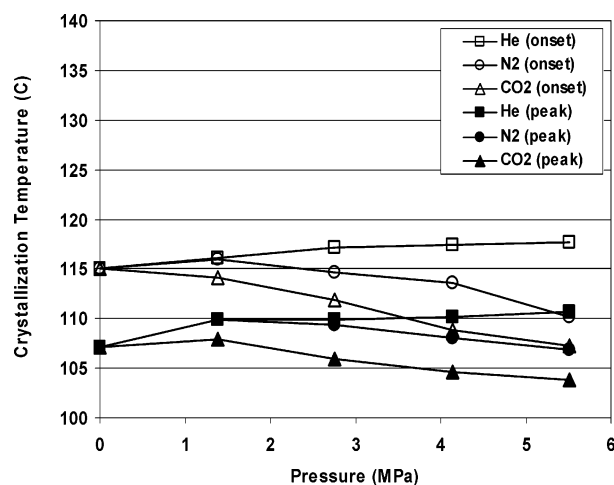**Figure 7.** Design of the cooling system for the high-pressure DSC cell.

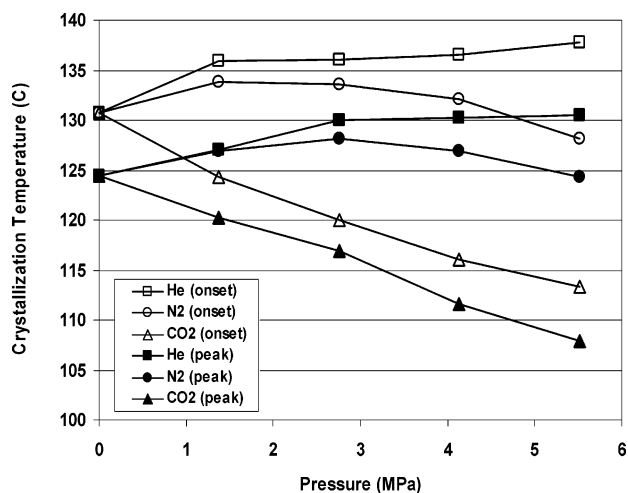**Figure 8.** Effects of pressure on the crystallization behavior of linear PP.

Figure 9. Effect of pressure on the crystallization behavior of branched PP.

sure was quite different for different gases. It was obvious that the gas at high pressure significantly affected the crystallization kinetics of the PP materials. As a gas permeates into the polymer matrix under high pressure, the dissolved gas may change the rate of
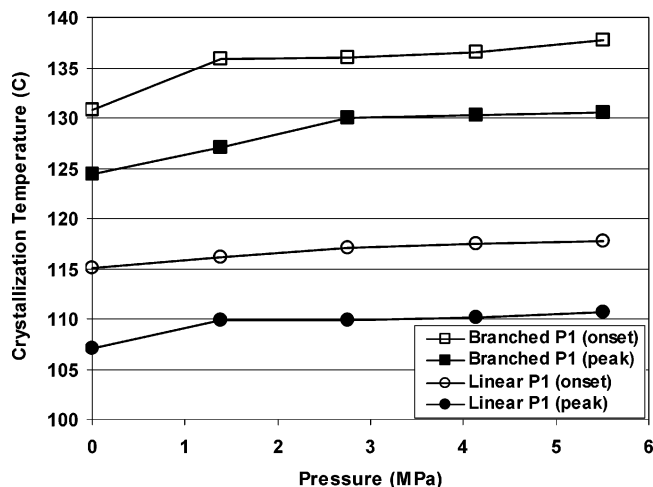
Figure 10. Effects of hydraulic pressure on the crystallization behaviors of linear and branched PP.

Figure 11. Effects of dissolved N_2 on the crystallization behaviors of linear and branched PP.

solved in the polymer increases with an increase in pressure,[41] the magnitude of the change in the plasticization and crystallization will be more pronounced at a higher pressure.

On the other hand, the crystallization kinetics will also be affected by the hydraulic pressure applied externally by the gas on the polymer melt. When the solubility of the gas in the polymer is very low or negligible, the kinetics of crystallization will be governed by the hydraulic pressure. However, when the solubility of the gas in the polymer is considerably high, both the hydraulic pressure and the dissolved gas will play their roles during the crystallization process in high-pressure experiments. The effect of dissolved gas on the crystallization kinetics can then be extracted by subtracting the effect of the hydraulic pressure from the overall crystallization behavior of the materials under high pressure.

Effect of Hydraulic Pressure. The effect of hydraulic pressure on the crystallization behaviors of PP materials was determined from the high-pressure experiments with He. Because the solubility of He in a polymer is very low, typically 1 order of magnitude lower than that of N_2 and 2 orders of magnitude lower than that of CO_2,[42] the effect of the dissolved He in a polymer melt would be negligible. Therefore, any change in the crystallization kinetics under an elevated pressure of He can be considered as the effect of hydraulic pressure.

Figure 10 shows the onset and peak crystallization temperatures as a function of the He pressure. It was noted that, by increasing the pressure in the DSC cell, the onset and peak crystallization temperatures increased for both the linear and the branched PP resins. The crystallization onset and peak temperatures for the branched PP increased by about 6 °C when the pressure increased from the atmospheric pressure to 5.5 MPa. However, for linear PP, the temperatures increased by only about 3 °C for the same amount of pressure change. As the hydraulic pressure in the DSC cell increases, the mobility of the polymer matrix molecules would decrease, and hence would accelerate the crystallization process, resulting in a higher crystallization temperature. Figure 10 also shows that the increase of the crystallization temperature for the branched PP was even more pronounced than that of linear PP.
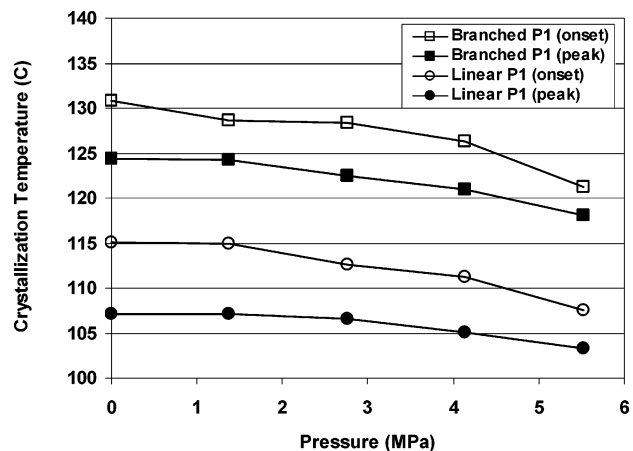
no further effects of hydraulic pressure were observed at higher pressures. It was not clear if the plateau region observed was due to the dissolved He in the PP materials at elevated pressures, or this showed the actual effect of hydraulic pressure on the crystallization behavior. This issue will be clarified, once the solubility of He in PP resins is measured.

Effect of Dissolved N_2. The effects of dissolved N_2 on the crystallization behaviors of linear and branched PP materials were extracted by subtracting the hydraulic pressure effects (Figure 10) from the overall thermograms (Figures 8 and 9). Figure 11 shows the onset and peak crystallization temperatures as a function of the N_2 pressure. N_2 has a relatively higher solubility than He,[42] and, therefore, the effects of dissolved gas with N_2 on the crystallization kinetics of PP materials are more pronounced as compared to the case of He.

It was observed that the onset and peak crystallization temperatures did not change much at low pressures below 1.4 MPa. Because the solubility of N_2 in the polymer is very low at a low pressure range, the overall crystallization behaviors in the low pressure range were mainly governed by the hydraulic pressure effect as shown in Figures 8 and 9. Although the effect of dissolved N_2 on the crystallization was negligible at a lower pressure, it was more pronounced at a higher pressure. Above 1.4 MPa, the onset and peak crystallization temperatures decreased moderately all of the way to 5.51 MPa.

It should be noted that these compensated results shown in Figure 11 may have some errors due to the dissolved He in the PP matrix at high pressures, which caused an incorrect hydraulic pressure effect. However, it is believed that the margin of error in the crystallization kinetics is insignificant.

Effect of Dissolved CO_2. As in the case of N_2, the effects of dissolved CO_2 on the crystallization behaviors of the linear and branched PP materials were extracted by subtracting the hydraulic pressure effect (Figure 10) from the overall thermograms (Figures 8 and 9). Figure 12 shows the onset and peak crystallization temperatures for linear P1 and branched P1 as a function of the CO_2 pressure. It was observed that the dissolved CO_2 suppressed the crystallization of the PP materials significantly. The decreased crystallization temperature due to the dissolved CO_2 was more pronounced in the thermogram of the branched PP as compared to linear

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