**Dilatometry: A Tool to Measure the Influence of Cooling Rate and Pressure on the Phase Behavior of Nucleated Polypropylene**

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The pressure and cooling rate dependence of the phase diagram of isotactic polypropylene (iPP) with the nucleating agent 1,3:2,4-bis(3,4-dimethylbenzylidene)-sorbitol (DMDBS) is investigated. A custom designed dilatometer is used to measure the specific volume of the blends for a wide range of cooling rates and elevated pressures. The crystallization line in the phase diagram shifts to higher temperatures with increase in the pressure and decrease in the cooling rate, independent of the concentration. The influence of cooling rate and pressure is related to the final morphology determined from X-ray diffraction. Dilatometry can be used as an interesting alternative to extract information on the phase behavior and crystallinity, for conditions hard or not at all obtainable with standard techniques like DSC or SALS.

**Introduction**

In injection molding a molten polymer is transferred into a mold, cooled, and solidified, all taking place at the same time. During the packaging stage, after injection, the polymer cools down under a high pressure and the material’s volume changes due to thermal shrinkage and crystallization in the case of semi-crystalline polymers, determining the product’s dimensions and dimensional stability. Predicting shrinkage needs accurate monitoring of the specific volume during processing.

Two types of experimental set-ups have been developed to measure changes in volume \( V \) as a function of pressure \( p \), and temperature \( T \), so-called pVT behavior, and these dilatometers are based on either the principle of confining fluid (CF) or confined compression (CC). Devices using the CC principle are called Piston-Die (PD) dilatometers, where the polymer is placed in a rigid cylinder or die, while a closely fitted piston is used to close off and pressurize the sample and to monitor volumetric changes. In CF dilatometers the sample is in a rigid cell surrounded by fluid, necessarily inert to the polymer, to which a hydrostatic pressure is applied. A flexible wall or bellows closes the chamber and the deformation of this wall is used to measure volume changes of both the fluid
and polymer. The advantage of the CF-type dilatometers is that a true hydrostatic pressure can be applied to the sample. Disadvantage is the use of a confining fluid, which requires proper sealing of the chamber. Moreover, studying the influence of (shear) flow is not possible using a CF-dilatometer.\textsuperscript{[4–6]} PD dilatometers generally have a much simpler design, but the main disadvantage is the friction force between cylinder wall and polymer in the solid state preventing a true hydrostatic pressure in this stage of the experiments.

We developed a PD-dilatometer that indeed fulfills requirements of realizable conditions similar to those in injection molding.\textsuperscript{[7,8]} An extra feature of the device, absent in the other dilatometers, is the possibility of applying shear with a rate of $O(10^{3}) \text{ s}^{-1}$ to the polymer prior to, or during, crystallization. Improvements over the years were aimed at downsizing and finally a table-top apparatus resulted.\textsuperscript{[9]}

Specific volume can be measured as a function of pressures (up to 1,000 bar), temperatures (up to 300 °C), cooling rates (up to 100 °C s$^{-1}$) and shear rates (up to 200 s$^{-1}$). The device has already been used to study the influence of molecular weight on the specific volume of isotactic polypropylene (iPP)\textsuperscript{[7,10]} and the effect of ethylene on the specific volume of propylene/ethylene random copolymers (P/E RACOs) under different processing conditions.\textsuperscript{[11]}

Here, the influence of the addition of nucleating agents, used in industrial production processes to reduce cycle times, is investigated. Crystallites formed in the presence of nucleating agents are smaller in size and larger in number, and are created at higher temperatures leading to a large lamellar thickness, which all contribute to improvements in mechanical and optical properties. Examples of such additives that work for iPP are sorbitol derivatives\textsuperscript{[12]} which in relatively small amounts ($\sim$0.2 wt.-%) enhance clarity and give rise to an increase in yield stress.\textsuperscript{[13,14]} Recently, a series of improved, much more effective nucleating agents have been developed yielding the same effects but now using concentrations as low as 0.02 wt.-%.\textsuperscript{[15,16]} These low molecular weight, polar, disc-like, self-organizing, and self-staggering organic compounds dissolve at high temperatures into the iPP melt which improves their dispersion. During cooling the additive phase separates and self-organizes into microfibrillar structures (L-S) forming a network in the polymer melt.\textsuperscript{[17–19]} X-ray studies by Thierry et al.\textsuperscript{[17]} and Balzano et al.\textsuperscript{[19]} showed that these fibrils have a nearly endless length and a radius of 5–10 nm. The addition of 1,3:2,4-bis(3,4-dimethylbenzylidene)-sorbitol (DMDBS) increases the crystallization temperature for iPP ($T_{c}$) with $\sim$20 °C and alters the rheology of the system during and after phase separation. The DMDBS concentration determines both the temperature of network formation and the increase in storage modulus, which can be more than one decade for 1 wt.-% DMDBS. The presence of the DMDBS network introduces long relaxation times and this slows down relaxation. Fibrils of the transient network can slide past each other when flow is applied and remain oriented for a very long period of time after the flow has been stopped. This has major consequences for the morphology development in a product. Flow above the (L-S) phase separation temperature leads to isotropic structures, due to a random spatial distribution of the DMDBS fibrils formed later. Flow after phase separation and network formation orients the fibrils, and thus also the resulting crystals that radially grow from the fibril surfaces.\textsuperscript{[17,19–22]}

So far, studies are performed at atmospheric pressure and relatively low cooling rates (O(10) °C min$^{-1}$) and the question arises how the iPP-DMDBS blends will behave when the pressure is increased to levels experienced in processing. The focus is on changes in the phase diagram of iPP-DMDBS at increased pressures and at high cooling rates. We will use dilatometry on the iPP-DMDBS systems used by Balzano et al.\textsuperscript{[19,22]} to study the influence of DMDBS concentration, cooling rate, and pressure on the evolution of specific volume, approaching processing conditions as experienced in injection molding, and to determine the phase diagram at elevated pressures. Crystallization and melting behavior under quiescent conditions and ambient pressure are determined using standard differential scanning calorimetry (DSC) and the results are used to check the mixing quality, to find the proper concentration regimes, and to act as a reference for the dilatometer results. It is demonstrated that dilatometry can be used to find the system’s phase behavior for conditions hard or not obtainable at all DSC, which is definitely the case when flow is applied. The phenomena observed are interpreted in terms of information on the resulting structure obtained by X-ray diffraction.

### Experimental Part

#### Materials

A commercial iPP grade was used (Borealis HD120MO) with a weight average molecular weight ($M_{w}$) of 365 kg mol$^{-1}$ and a polydispersity (PD) of 5.2, identical to that used in several studies.\textsuperscript{[7,8,10,19,22–24]} The nucleating agent DMDBS (Millad 3988, Milliken Chemical, Belgium) is a powder and used as received.

#### Sample Preparation

Prior to blending, the polymer pellets were pulverized in a freezer mill cooled with liquid nitrogen (Retsch ZM100, F. Kurt Retsch GmbH & Co. KG, Germany). Various dry-blended mixtures of i-PP and 0.3, 0.7, and 1.0 wt.-% DMDBS were compounded in a laboratory, corotating mini-twin-screw extruder (DSM Xplore 15 ml microcompounder) in a nitrogen atmosphere for 10 min at a temperature of 240, 250 and 260 °C, respectively. The tempera-
tures were determined from the melting temperature/composition diagrams of the system i-PP/DMDBS. The solidified strings of material from the extruder were chopped into pellets and fed into the hopper of a Babyplast mini-injection molding unit with which sample rings with a mass of ~50 mg were produced, with an outer and inner diameter of 22 and 21 mm, respectively, giving a wall thickness of 0.5 mm, and a height of 2 mm. The samples are coded ‘PP’ plus the concentration, e.g. PP0 for the pure polymer and PP07 for the blend with 0.7 wt-% DMDBS.

**Differential Scanning Calorimetry (DSC)**

Crystallization and melting behavior of the pure polymer and the three binary blends was studied under quiescent conditions on a Mettler Toledo DSC (DSC823e). The peak melting temperature, $T_m$, and peak crystallization temperature, $T_c$, were determined using a heating and cooling rate of 10 °C min$^{-1}$ on samples with a weight of 3 ± 0.5 mg in a nitrogen atmosphere. The start and end temperature are 25 and 230 °C, respectively, at which the sample is kept for a time period of 5 min. The results are used to compare with Balzano et al. [19] to check for good mixing and proper concentrations.

**Dilatometry**

Dilatometer experiments were performed with the custom made PD-dilatometer, see Figure 1 for a schematic drawing of the pressure cell. The measurements were carried out in the isobaric cooling mode. A high accuracy displacement transducer is used that, however, only has a limited range of ±1 mm. Therefore, two measurements using two different glass pins are needed, one without the sample (baseline run) and one with the sample (experimental run). The consequence is that the apparatus has no absolute zero position and the resulting volume is relative. To obtain the absolute value, i.e. to determine the missing constant, the data obtained are calibrated with a curve obtained from a CF-dilatometer, measured under the same conditions (Equation 1).

$$\Delta x = \frac{\Delta X A}{m} + C = \frac{(x_1 - x_2)\pi(r_0^2 - r_i^2)}{m} + (v_{220\,\text{C,CF}} - v_{220\,\text{C,PD}})$$

In Equation 1, $v$ is the absolute specific volume, $\Delta X$ the difference in displacement measured in the experimental run ($x_1$) and the baseline run ($x_2$), $A = \pi(r_0^2 - r_i^2)$ the cross-section area of the sample ring with $r_0$ and $r_i$ the outer and inner radius, respectively, $m$ the mass of the sample and $C$ is a constant defined as the difference between the specific volume measured in a CF-dilatometer ($v_{220\,\text{C,CF}}$) and the one obtained with the PD-dilatometer ($v_{220\,\text{C,PD}}$) at 220 °C. The following procedure is adopted for all measurements, as graphically represented in Figure 2:

- The sample is heated at a rate of 10 °C/min to 230 °C.
- Next, it is kept at this temperature for 10 min to erase all previous processing history.

During the last step, a shear flow can be applied at any desired temperature. The cooling medium used, and the flux of this medium, determines the cooling rate, which is time-dependent. Cooling rates

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1 In the latest version of the apparatus (second half 2008) this problem is overcome.
Wide angle X-ray diffraction (WAXD) single-shot experiments were performed at the Dutch-Belgian (DUBBLE) beamline BM26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The size of the X-ray beam is 100 μm having a wavelength of 1.03 Å. A FRELON detector is used with 2048 × 2048 pixels with both a horizontal and vertical pixel size of 14 μm. From the diffraction patterns the degree of crystallinity and the type and amount of crystal phase is determined.

Results and Discussion

DSC

The measured peak melting and crystallization temperatures are summarized in Table 1. The results compare well to those obtained by Balzano et al.\textsuperscript{[19]} \( T_c \) is increased almost 20 °C by the addition of 0.3 wt.-% DMDBS and remains unaltered with increase in the concentration. This means that the nucleating efficiency saturates already at low concentrations,\textsuperscript{[21]} but mechanical and optical properties are sometimes still improving. Careful examination of the cooling thermograms also reveals a small peak related to the crystallization of DMDBS; thus at this temperature, indicated by \( T_{ps} \) (Table 1), the system phase separates. With the DSC data a phase diagram can be built in which three regions are identified\textsuperscript{[13,19]} shown in Figure 3. At high temperatures, DMDBS is dissolved in the iPP melt forming a homogeneous solution (region I). Cooling leads to the phase separation of DMDBS (region II) on top of which the polymer crystallizes during a further temperature decrease (region III).

Specific Volume

Dilatometer experiments are performed at 100, 400, and 600 bar and three different cooling profiles. Temperatures are recorded at six positions outside the sample at both the inner and outer sample surfaces, inside the piston and die, respectively (Figure 1). The corresponding average sample temperature, \( T_c \), is determined using a heat conduction analysis. As mentioned, cooling rates given are average values during the crystallization of the polymer. An alternative value for the cooling rate, often used, is the value obtained at a temperature of 70 °C, \( T_{70} \), which is regarded characteristic for iPP since at this temperature the maximum in overall crystallization rate is found.\textsuperscript{[25–28]} Both the values of \( T_c \) and \( T_{70} \) are given in Table 2.

Figure 4 shows the specific volume of PP0 as a function of temperature and pressure, measured at the three different cooling rates. With an increase in the pressure, crystallization starts at a higher temperature due to an increase in the equilibrium melting temperature, \( T_m^c \).\textsuperscript{[29]} Undercooling, defined as \( \Delta T = T_m^c - T \), is the driving force

Table 1. DSC characteristics of the pure polymer and the three blends: melting temperature, \( T_m \), crystallization temperature, \( T_c \), and phase separation temperature, \( T_{ps} \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_m ) (°C)</th>
<th>( T_c ) (°C)</th>
<th>( T_{ps} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP0</td>
<td>163</td>
<td>114</td>
<td>–</td>
</tr>
<tr>
<td>PP03</td>
<td>165</td>
<td>132</td>
<td>158</td>
</tr>
<tr>
<td>PP07</td>
<td>165</td>
<td>132</td>
<td>180</td>
</tr>
<tr>
<td>PP10</td>
<td>165</td>
<td>133</td>
<td>189</td>
</tr>
</tbody>
</table>

Table 2. Average cooling rate during crystallization and cooling rate at 70 °C, \( T_{70} \), for the different cooling media.

<table>
<thead>
<tr>
<th>Cooling medium</th>
<th>( T_c ) (°C s(^{-1}))</th>
<th>( T_{70} ) (°C s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surrounding air</td>
<td>( T_{low} )</td>
<td>0.1</td>
</tr>
<tr>
<td>Pressurized air</td>
<td>( T_{medium} )</td>
<td>1.5</td>
</tr>
<tr>
<td>Water</td>
<td>( T_{high} )</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 3. Phase diagram of the iPP-DMDBS system (0–1 wt.-%) obtained on cooling using DSC data: (■) crystallization temperature, \( T_c \), and (○) phase separation temperature, \( T_{ps} \) (Table 1).
for crystallization, and hence, since crystallization starts at the same amount of undercooling, an increase in $T_0$ with pressure leads to a shift to a higher crystallization (onset) temperature. With an increase in the cooling rate, the transition in specific volume that marks the crystallization of the polymer shifts toward lower temperatures and becomes less sharp to ultimately stretch over a wide range of temperatures at the highest cooling rate.\cite{3,6,30} Moreover, when there is less time to form new nuclei and to grow them into spherulites, the crystallization process is suppressed.\cite{30} The values of the specific volume in the solid state are sometimes less reliable, see for instance Figure 4(c) at 400 bar, due to wall friction between sample and cell, although grease is applied. The results for PP03 are displayed in Figure 5 and similar behavior as for PP0 is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Influence of cooling rate on the specific volume of PP0 measured at 100 bar (\textcircled{1}), 400 bar (\textcircled{2}), 600 bar (\texttriangle); (a) 0.1 °C s$^{-1}$, (b) 1.5 °C s$^{-1}$, (c) 30 °C s$^{-1}$. Solid lines in (b) are specific volume of the amorphous phase as described by a Taylor series (Equation 8).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5}
\caption{Influence of cooling rate on the specific volume of PP03 measured at 100 bar (\textcircled{1}), 400 bar (\textcircled{2}), 600 bar (\texttriangle); (a) 0.1 °C s$^{-1}$, (b) 1.5 °C s$^{-1}$, (c) 30 °C s$^{-1}$.}
\end{figure}
found: The polymer starts to crystallize at higher temperatures with an increase in the pressure and a decrease in the cooling rate. However, due to the presence of the DMDBS nucleating agent, the onset of crystallization shifts to higher temperatures and the transition is more sharp.\(^{[13,19]}\)

This is more clearly illustrated in Figure 6, which shows specific volume as a function of temperature measured for all four DMDBS concentrations used, at different cooling rates, at a pressure of 400 bar. The specific volume in the solid state is reproducible and deviations due to wall friction, mentioned above, are incidental. Above 0.3 wt-% of DMDBS, the nucleating efficiency saturates and the crystallization temperature is equal for PP03, PP07, and PP10. This is also observed using DSC\(^{[13,19]}\) and small-angle X-ray scattering\(^{[19]}\) for the same iPP-DMDBS systems.

The crystallization temperature, \(T_c\), of the dilatometry measurements is defined using the steepest slope; thus it is the temperature, where \(d\nu/dT\) obtains its highest value, see Figure 7, showing the derivative of the results from Figure 4(b). In this example, the peak is found at 122 °C. Results for all processing conditions applied are summarized in Table 3 and Figure 8.

With the addition of DMDBS the increase in \(T_c\) is found to be approximately 15 °C. For PP0, we find a pressure dependence on \(T_c\) at the lowest cooling rate of 0.026 °C bar\(^{-1}\), which compares well with values for iPP reported in the literature.\(^{[29–32]}\) The value does not change with the addition of DMDBS. The influence of pressure on the crystallization temperature is independent of the cooling rate; only at the highest cooling rate a slight increase is detected to a value of 0.033 °C bar\(^{-1}\) for the.

### Table 3. Crystallization temperatures, \(T_c\), for all processing conditions applied.

<table>
<thead>
<tr>
<th>(p) [bar]</th>
<th>PP0</th>
<th>PP03</th>
<th>PP07</th>
<th>PP10</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>124</td>
<td>140</td>
<td>140</td>
<td>138</td>
</tr>
<tr>
<td>400</td>
<td>133</td>
<td>147</td>
<td>148</td>
<td>147</td>
</tr>
<tr>
<td>600</td>
<td>137</td>
<td>152</td>
<td>153</td>
<td>153</td>
</tr>
<tr>
<td>100</td>
<td>116</td>
<td>131</td>
<td>133</td>
<td>131</td>
</tr>
<tr>
<td>400</td>
<td>124</td>
<td>138</td>
<td>141</td>
<td>141</td>
</tr>
<tr>
<td>600</td>
<td>126</td>
<td>139</td>
<td>144</td>
<td>144</td>
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<tr>
<td>100</td>
<td>108</td>
<td>126</td>
<td>126</td>
<td>128</td>
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<tr>
<td>400</td>
<td>118</td>
<td>132</td>
<td>136</td>
<td>139</td>
</tr>
<tr>
<td>600</td>
<td>121</td>
<td>143</td>
<td>143</td>
<td>144</td>
</tr>
</tbody>
</table>
samples containing DMDBS, although at high cooling rates the transition is less distinct. Figure 8 shows the pressure and cooling rate dependence of the phase diagram reported in Figure 3, at least of the crystallization line separating regions II and III. The phase separation line, $T_{ps}$, between regions I and II in Figure 3, is not detected as a change in volume, either because there is no volume change or the method applied is not sufficiently sensitive. Balzano et al.\textsuperscript{[19]} showed that flow below $T_{ps}$ orients DMDBS fibrils and templates this orientation to the polymer lamellae growing on top, where flow above $T_{ps}$ has no orientation effect. Lamellar orientation can be detected ex situ with SAXS and therefore, to investigate the effect of pressure on $T_{ps}$, we suggest the following procedure, illustrated in Figure 9(b):

- Cool the melt to a temperature, $T_g$, just below $T_{ps}$. Assuming the same pressure dependence as for $T_c$, the temperature $T_{ps,p}$ indicated with a dashed line in the phase diagram (Figure 9(a)), is a correct estimate.
- Allow DMDBS to phase separate, self-organize, and crystallize into fibrils at this temperature.
- Apply flow at $T_g$ to orient the fibrils.
- Cool to room temperature.
- Measure lamellar orientation with SAXS.

When lamellar orientation is present, $T_{ps,p}$ is apparently above the flow temperature, $T_g$. Next we increase $T_g$ until no lamellar orientation is measured anymore, to determine $T_{ps,p}$. When no orientation is detected in first instance, $T_g$ has to be lowered. Because only a low shear rate, $\gamma$, is necessary to orient the DMDBS fibrils, stretching of polymer chains that results in shish formation and corresponding oriented lamellar growth (kebabs) can be detected. Furthermore, the dilatometric data in Figure 8 shows an increase of the crystallization temperature $T_c$ with pressure, which is in agreement with the seen pressure dependence of $T_{ps}$. The dashed line indicates the expected shift of the phase separation line. (b) Suggested procedure to detect pressure dependence of $T_{ps}$.
avoided. An alternative to measure $T_{ps,p}$ is the use of a pressure cell in combination with in situ X-ray scattering.

The influence of cooling rate ($T_{70}$) on density, $\rho$, and morphology of iPP at ambient pressure has been studied even for cooling rates up to 1000 °C s$^{-1}$. The density slowly decreases with increase in the cooling rate, until a steep drop is found for cooling rates above 50 °C s$^{-1}$ to approach a density plateau. At low cooling rates only the stable $\alpha$ (crystal) and amorphous phases are formed and the decrease in density relates to a decrease in the $\alpha$ phase, increasing the amorphous part. At intermediate cooling rates, the density decreases rapidly, given the competition between $\alpha$ and mesomorphic (a crystalline phase with a low range order) phases. In the plateau region at high cooling rates, the mesomorphic and amorphous phases dominate and dictate the polymer’s density. Our range of cooling rates is limited with a maximum value of $T_{70} = 12$ °C s$^{-1}$. If we calculate density from our measurements as $\rho = 1/\nu_{50}$, the inverse of specific volume at the end temperature of 50 °C, a gradual decrease with the logarithm of the cooling rate is observed, indeed as in the first cooling rate regime, see Figure 10 that shows data for PP03. Small deviations in density are due to some wall friction, which makes the specific volume in the solid state in some experiments less reliable. Density increases with an increase in the pressure, which is opposite to the pressure dependence of $\rho$ reported by La Carrubba et al., who observed $\rho$ to decrease with pressure, and similar results were obtained by Van der Beek et al. The contradiction finds its reasoning in that the density values reported by La Carrubba et al. and Van der Beek et al. are measured in a density gradient column at ambient pressure, after crystallization at elevated pressures. They explained the decrease in density with pressure by a decrease in $\alpha$ crystal phase and an increase in mesomorphic phase. In our situation, density is determined in situ at the pressure at which the material crystallized and compressibility of the samples is included in the density values. Their results should be interpreted as the density of an injection molded product after mold release, while ours provide the product’s density within the mold during the packing stage.

**WAXD**

Only samples prepared at the intermediate cooling rate ($T_{medium} = 1.5$ °C s$^{-1}$) are analyzed using X-ray diffraction. Patterns are air scattering corrected, circular integrated, and normalized by defining the total area equal to 1. Figure 11(a) shows an example of a WAXD profile of the pure polymer, PP0, crystallized at a pressure of 400 bar. The shaded area is the amorphous halo, measured on a quenched, low tacticity sample (37% mmmm) with negligible crystallinity and scaled to the minimum between the (110) and (040) diffraction peaks. The
degree of crystallinity, $x_c$, is determined using

$$x_c = \frac{A_c}{A_{\text{total}}}$$

(2)

with $A_c = A_{\text{total}} - A_g$ being the area of the crystalline peaks, $A_{\text{total}}$ the area of the total pattern and $A_g$ that of the amorphous halo. Crystallinity as a function of DMDBS concentration and pressure is given in Figure 11(b) and clearly the overall crystallinity is almost constant, for all DMDBS concentrations and pressures applied ($\sim$68–70%) and typically for the pure polymer 2–3% lower than for the samples containing DMDBS, in agreement with data of comparable iPPs.\cite{34,39}

Next we focus on the type of crystals formed. In iPP polymorphism is common and the polymer can crystallize into different types of crystal phases, the $\alpha$, $\beta$, $\gamma$ and mesomorphic phase. Under standard conditions the $\alpha$ phase, with a monoclinic crystal structure, is formed, characterized by the so-called cross-hatching or lamellar branching.\cite{40,41,42,43,44,45} Consisting of daughter lamellae that grow on top of the initial (mother) lamellae under an angle of $\sim$80° or 100°. The $\beta$ phase, with its hexagonal unit cell, is formed when the polymer crystallizes (i) in the presence of a temperature gradient,\cite{42} (ii) under conditions like a strong imposed orientation,\cite{69,70} and (iii) in the presence of certain nucleating agents.\cite{46,47,48,49,50} Occurrence of the $\gamma$ phase, with its orthorhombic unit cell, is controlled by the molecular structure: (i) low stereo-regularity of the chains,\cite{40,41,42} (ii) a low molecular weight\cite{50} and (iii) copolymerization with for instance ethylene.\cite{51} Also in crystallization at elevated pressures $\gamma$ crystal structures are sometimes observed.\cite{51,34,35} Finally, the mesomorphic crystal phase is only found when the polymer is cooled very rapidly.\cite{27,36}

The different crystal types have their own specific crystal planes with a specific d-spacing between the planes and thus a specific WAXD pattern.\cite{52,53,54,55} Most of the diffraction peaks of the different crystal phases overlap, and have almost the same diffraction angle, but for each phase one peak can be attributed to be specific, identified as the (130)$_{\alpha}$, the (300)$_{\beta}$ and the (117)$_{\gamma}$ peak. These reflections are used to determine the fraction of different crystal types and several methods are applied, either to determine the fraction of $\alpha$ and $\beta$ phase\cite{55,56} or of $\alpha$ and $\gamma$ phase.\cite{34,35,57} These methods work as long as the third crystal type, either $\gamma$ or $\beta$ respectively, is not present. Some methods use the area under the peaks,\cite{34,56} others the height of the peaks.\cite{34,55,57} We use the first and define the fraction of crystallinity ($x_i$) of a specific crystal type as

$$x_i = \frac{A_i}{A_\alpha + A_\beta + A_\gamma} x_c$$

(3)

with $i$ being the specific crystal phase (either $\alpha$, $\beta$, or $\gamma$) and $A_i$ the area under the peak of the specific phase. In all of our samples, the $\beta$ phase is absent and Equation 3 thus simplifies to

$$x_i = \frac{A_i}{A_\alpha + A_\gamma} x_c$$

(4)

with $i$ either $\alpha$ or $\gamma$. Most of the peaks partially overlap, which makes exact determination a little more difficult, and Figure 12 illustrates the method used, following Van der Burgt et al.\cite{34,35}

Figure 13(a) shows the scattering patterns of samples measured at a pressure of 400 bar. The addition of DMDBS, like pressure,\cite{31,34,35} see Figure 13(b), promotes the formation of the $\gamma$ phase. Fractions of the $\alpha$ and $\gamma$ phase crystals are determined using Equation 4 and displayed in Figure 14. Due to the presence of the nucleating agent, the polymer crystallizes at higher temperatures where nucleation of $\gamma$ phase crystals is favored, which can be explained from a thermodynamic point of view.\cite{51} The temperature at which the polymer crystallizes increases with pressure, which also contributes to the formation of the $\gamma$ phase.

**Crystal Structure and Specific Volume**

In DSC, the measure to monitor crystallization is the heat released by the crystallizing polymer. Crystallinity from DSC is determined by comparing the melting enthalpy of a sample, $\Delta H$, which is the area under the melting trace, to the melting enthalpy of a 100% crystalline sample, $\Delta H_{100\%}$ ($=209$ J g$^{-1}$ for iPP\cite{58,59})

\[
\frac{\Delta H}{\Delta H_{100\%}} \times 100\% = x_c
\]

(5)
In dilatometry, crystallization is measured as the volume change of the material, i.e. a transition from melt to solidified polymer. The Clapeyron relation (Equation 6) describes the slope, $\frac{dp}{dT}$ of the line separating two phases of matter, e.g. liquid and solid, in a pressure–temperature diagram:

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V}$$

with $\Delta H$ being the latent heat, $T$, the temperature, and $\Delta V = v_a - v_c$, the volume change of the phase transition, i.e. the difference in specific volume of the amorphous phase, $v_a$, and the crystalline phase, $v_c$. In the rewritten form (Equation 7), it is used to derive the melting enthalpy, and in our case the crystallization enthalpy, $\Delta H = \Delta H_c$, from dilatometry for different polymers:[60–62]

$$\Delta H = \frac{T \Delta V}{dT/dp}$$

For the temperature, the crystallization temperature, $T_c$, is used and $dT/dp$ is determined to be 0.0268°C/bar (Figure 8, Section 3). The specific volume of the amorphous melt ($i = a$) and the solid phase ($i = s$) are described as a Taylor series in pressure and temperature:[8]

$$n_i = n_{ref, i} + \frac{\partial n_i}{\partial T} \Delta T + \frac{\partial^2 n_i}{\partial p^2} \Delta p^2 + \frac{\partial^2 n_i}{\partial T \partial p} \Delta T \Delta p$$

$$\Delta T = T - T_{ref}$$

$$\Delta p = p - p_{ref}$$

with $T_{ref} = 0$°C and $p_{ref} = 20$ MPa. The partial derivatives for the Taylor series given by Van der Beek et al.[8] provide a good description for the amorphous part (see Figure 4(b)), but in the solid state it fails, most probably due to a wrong value of one (or more) of the partial derivatives. Here, the specific volume of the solid state is determined, for every pressure separately, using a linear dependence on temperature. Because the solidified polymer is semi-crystalline and consists partially of amorphous regions, the specific volume of the crystalline fraction, $v_c$, is determined from X-ray diffraction studies.[60–62] Here, another method is applied. The specific volume can be described by a combination of the specific volumes of the two phases present, which are not influenced by each other[6]

$$v = \xi_g \chi_c v_c + (1 - \xi_g \chi_c) v_a$$

in which $\xi_g$ is the degree of space filling and $\chi_c$ the end level of crystallinity. In the solid state, $v = v_s$, the degree of space filling, $\xi_g = 1$ and $v_c$ and $\Delta V$ can be derived as,
respectively
\[ v_c = \frac{1}{\chi_c} (v_s - (1 - \chi_c)v_a) \] (12)
and
\[ \Delta v = \frac{1}{\chi_c} (v_a - v_s) \] (13)

Crystallinity is not known and it is the quantity to be determined from \( \Delta H \), but can be replaced by the definition in Equation 5. Substitution of Eqs. 13 and 5 into Equation 6 and rewriting gives for the crystallization enthalpy
\[ \Delta H = \sqrt{T \Delta H_{100\%} (v_a - v_s)} \frac{d\nu}{dp} \] (14)

The determination of \( v_a \) and \( v_s \) at \( T_c \) is illustrated in Figure 15.

The crystallinity, determined from the obtained specific enthalpy using Equation 5, is shown in Figure 16. The results obtained with Equation 14 show a pronounced influence of the pressure and DMDBS content: the crystallinity (i) decreases with pressure, (ii) increases with the addition of DMDBS, independent of concentration and pressure, and (iii) decreases with cooling rate.[25–28,37,38] Crystallinity from dilatometry for the intermediate cooling is a little higher than the results obtained with WAXD (Figure 11) and, although observation (ii) is also observed using WAXD, the increase in crystallinity with decrease in the pressure and the addition of DMDBS is more pronounced for the dilatometry results. Some authors report a value of 234 J g\(^{-1}\) for the melting enthalpy of 100% crystalline iPP applying Equation 6[61], which is higher than the 209 J g\(^{-1}\)[58,59] and discussed to give good accordance with WAXD results.[63] Also the increase due to the addition of DMDBS is larger than observed using WAXD, but similar to the increase observed in DSC.[19] At the highest cooling rate (Figure 16(c)) the spread in \( \chi_c \) is larger, due to less distinct transition in specific volume.

A remark has to be made to the application of the Clapeyron relation (Equation 6) to the iPP-DMDBS blends, because the relation characterizes a phase transition between two phases of matter of the same material. In the blends a second material, i.e. DMDBS, is present, and Equation 6 might not be applied rendering a stronger increase in crystallinity from dilatometry compared to the WAXD results.

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**Figure 15.** Illustration of the method for determination of \( v_a \) and \( v_s \).

**Figure 16.** Crystallinity, \( \chi_c \) determined from Equation 5 and 14 as a function of DMDBS concentration and pressure: 100 bar (○), 400 bar (□), 600 bar (△), filled symbols: \( \chi_c \) values from WAXD (intermediate cooling rate, Figure 11(b)); (a) 0.1 °C s\(^{-1}\), (b) 1.5 °C s\(^{-1}\), (c) 30 °C s\(^{-1}\).
Conclusions

The influence of the amount of nucleating agent, DMDBS, present on the evolution of the specific volume of isotactic polypropylene, iPP, at different cooling rates and at elevated pressures has been investigated, using dilatometry. In general, the addition of DMDBS has pronounced influence on the evolution of the specific volume. Especially the crystallization line in the iPP-DMDBS phase diagram, that marks the transition in specific volume, is affected. Above the minimum concentration of 0.3 wt.-%, the effect of the nucleating agent becomes independent of concentration, and the crystallization line stays horizontal. Although the overall structure of the resulting crystalline morphology is greatly affected by the addition of DMDBS, the resulting specific volume hardly changes with processing conditions and shows a clear link to the degree of crystallinity, which is also only marginally influenced by the addition of DMDBS. DMDBS enhances the occurrence of the γ crystalline phase. The Clapeyron relation, used to derive the crystallization enthalpy from dilatometry measurements, renders satisfactory results for pure polypropylene, but overestimates crystallinity somewhat in the case of the nucleated iPP-DMDBS blends.

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