

Influence of Cooling Rate on pVT-Data of Semicrystalline Polymers

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ABSTRACT: For numerical simulations of the injection-molding process, an accurate description of the specific volume is needed to predict differential shrinkage during and after molding, which causes thermally induced stresses and controls the dimensional accuracy and long-term dimensional stability. For amorphous polymers, for which it can often be assumed that cooling-rate dependence can be ignored, standard techniques enable measurements of the specific volume as a function of temperature and pressure. For semicrystalline polymers, the situation is more complicated since the specific volume depends strongly on the degree of crystallinity, which itself depends on the thermomechanical history, that is, temperature and pressure (for quiescent crystallization). This requires the use of a combined experimental–numerical technique to interpret the data and to determine the specific volume. Standard equipment can only be used at relatively low cooling rates. Since high cooling rates are present during injection molding, improved experimental techniques must be designed. A setup based on the confining fluid technique is built, which can reach cooling rates to 60 Ks^{-1} and pressures to $20 \times 10^6 \text{ Pa}$. During an experiment, the specific volume is measured together with the temperature history and pressure. Using an accurate model to calculate the crystalline structure, together with a specific-volume model which depends on this structure, enables the determination of model parameters. Comparing both the measurements and the model predictions, leads to the conclusion that modeling of the crystallization kinetics results in accurate predictions of the specific volume. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1170–1186, 2001

Key words: specific volume; crystallization kinetics; high cooling rates

INTRODUCTION

In polymer processing, the specific volume plays a major role. It is influenced by processing characteristics like temperature, pressure, and flow history and it determines shrinkage, which expresses itself by dimensional (in)stability. For

amorphous polymers, the pressure and temperature history determine the specific volume. For semicrystalline polymers, however, the specific volume is also influenced by the crystalline structure. This structure itself is influenced by the pressure and the temperature history and by the configuration of the polymer chains and flow-induced ordering phenomena during flow as well. Consequently, for semicrystalline polymers, the specific volume has to be related to the pressure, temperature, cooling rate, and crystalline state (Zuidema et al.¹). For injection molding of amorphous polymers, Caspers² showed the need for

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accurate measurements and modeling of the specific volume because of its large impact on the results. When modeling the injection molding of semicrystalline polymers, the same high accuracy has to be achieved not only in relation to the pressure and temperature, but also to the cooling rate and ordered state of the molecules. This conclusion was subscribed to by Fleischmann and Koppelman,³ regarding the influence of the processing conditions on the specific volume.

Two different techniques are commonly applied when measuring the specific volume:

The piston-die technique: The material is enclosed and pressurized in a die using a piston. The volume of the material is registered during the measuring cycle using the displacement of the piston. Both temperature and pressure can be varied; however, the pressure applied is not hydrostatic because the material sticks to the wall (He and Zoller⁴). According to Zoller and Fakhreddine⁵ this technique only gives accurate results when the shear modulus of the material is much smaller than its bulk modulus, which is the case for polymer melts. However, when the degree of crystallinity increases, due to crystal growth in the sample, the material will behave more like a rubber/solid and measurements will become inaccurate. Other problems are the possible leakage between the piston and the die and the formation of voids in the sample when solidifying. The technique was, for instance, applied by Chang et al.⁶ who used a pVT-100 apparatus from SWO Germany.⁷

The confining fluid technique: The sample is enclosed in a sample cell containing a confining fluid. The cell is closed using a bellows, whose displacement is registered during a measuring cycle, giving the relative volume difference of the sample. The absolute specific volume can be obtained by correcting for the relative volume difference with the specific volume of the confining fluid. Both pressure and temperature can be varied. Moreover, the pressure is purely hydrostatic as the sample is surrounded by the confining fluid. Other advantages are the absence of leakage and friction problems. Problems with this technique are the possible interaction of the confining fluid with the sample. Most of the time, mercury is used as the confining fluid, although no published pVT data for mercury above about 463 K are available.⁵ The technique was, for instance, applied by Moldflow⁸ using a GNOMIX PVT testing apparatus.

With both techniques, two different measuring modes can be performed:

Isobaric mode: The volume is measured while a constant pressure is maintained and the temperature is varied, with a constant cooling or heating rate. When the temperature scan is completed, another pressure is selected and the temperature is varied again. If an increasing temperature scan is used, the initial crystal structure of the sample has to be known for semicrystalline polymers in order to have a reference point for the specific volume measured. For the piston-die technique, only a decreasing temperature sequence can be used since the material has to melt in order to fill the die completely.

Isothermal mode: The volume is measured at selected temperatures, while the pressure is varied. Again, using an increasing temperature scan, the initial crystal structure of the sample has to be known, and for the piston-die technique, only a decreasing temperature sequence can be used.

During a measuring cycle, a steady state in the material is assumed, which implies that cooling and heating rates are restricted to 0.83 Ks^{-1} at maximum in a DSC (He and Zoller⁴) and to 0.167 Ks^{-1} for the confining fluid or piston-die technique (due to the sample size). However, in injection molding, cooling rates depend on the thickness of the product. They change from very high values at the cavity walls to almost zero at the product core. For amorphous polymers, one could assume that the specific volume measured still holds at these high cooling rates; for semicrystalline polymers, however, it will certainly not. Consequently, these standard techniques (confining fluid and piston die) can only be used for amorphous polymers or at low cooling rates for semicrystalline polymers. Specific-volume measurements at low cooling rates were done by Douillard et al.⁹ ($\dot{T}_{\text{max}} = 0.333 \text{ Ks}^{-1}$), He and Zoller⁴ ($\dot{T}_{\text{max}} = 0.042 \text{ Ks}^{-1}$), and Ito et al.¹⁰ ($\dot{T}_{\text{max}} = 0.033 \text{ Ks}^{-1}$). The actual specific volume was measured during a cooling run. Sato et al.¹¹ measured the specific volume of a semicrystalline polypropylene and studied the effect of a sample cup holder and the sample form. Because crystallization kinetics were not included, direct and quantitative conclusions on the influence of the crystallization kinetics on the specific volume could not be drawn. Moreover, the absence of the influence of cooling rate in these measurements makes them inadequate for the use in injection-molding simulations.

An attempt to measure the specific volume of semicrystalline polymers at higher cooling rates was performed by Lobo and Bethard¹² using a combination of standard pVT and DSC measurements. DSC measurements were done on an injection-molded sample at the same heating rates as those in the pVT measurement. These were used in the analysis to calibrate the results from the DCS against the pVT apparatus. Isothermal measurements were first performed in the solid state over a wide temperature range using the pVT apparatus. Afterward, the melting behavior at low pressures was determined. High-cooling-rate DSC measurements were performed to determine the cooling-rate dependence of the crystallization transition. The pVT data were then constructed by piecing together the measured solid-state pVT data of the injection-molded part with the measured melt-state pVT properties using the cooling-rate-dependent crystallization transition. The maximum cooling rate applied was 1.667 Ks^{-1} . However, it was shown by Wu et al.¹³ that DSC curves cannot correctly be interpreted if internal heat-transfer problems of the DSC apparatus are ignored, and for cooling rates of 1.667 Ks^{-1} , the influence of the temperature difference in the sample on the measurements is severe. Similar conclusions were drawn by Piccarolo.¹⁴

To measure the specific volume of semicrystalline polymers at high cooling rates, a different technique has to be applied. Piccarolo¹⁴ measured the temperature at the sample surface during cooling of a sample from one side. The temperature distribution in the sample was calculated using the energy equation. After extracting the sample, the density distribution was measured using a density column. The structure of the sample was characterized using WAXD and optical microscopy. In this way, cooling rates up to $\dot{T} = 311 \text{ Ks}^{-1}$ were reached. However, since the specific volume is determined afterward, information on the crystallization process in the sample (expressed by the specific volume) was not obtained.

When numerical simulations are involved, a mathematical representation of the specific volume is necessary. Many models, like the Tait equation,¹⁵ assume that the specific volume depends only on the pressure and temperature. Modifying the Tait equation for cooling rate effects was done by Chang et al.⁶ The resulting set of equations holds only for amorphous polymers at a maximum cooling rate of approximately

0.167 Ks^{-1} , and Zoller¹⁶ showed that, on the one hand, the Tait equation does not yield a good representation of the compressibility behavior of solid semicrystalline polymers like polypropylene, but, on the other hand, semicrystalline polymer melts are represented well. Ito et al.¹⁷ adopted the specific-volume equation for polystyrene proposed by Spencer and Gilmore,¹⁸ which is based on the van der Waals equation, to describe the specific volume of the isotactic polypropylene used. The specific volume is divided into three states (melt, crystallization, and solid), with the knee points obtained from crystallization kinetics calculated at the actual cooling rate. Although this results in a first-order approximation for the specific volume of a semicrystalline material, the actual crystallization kinetics are not included thoroughly. Crystallization kinetics equations were incorporated by Hieber,¹⁹ who used a two-domain Tait equation for the asymptotes at high and low temperatures. The specific volume at the transition was calculated using the Nakamura equation for crystallization kinetics and a linear interpolation from one asymptote to the other. For cooling rates up to 0.04 Ks^{-1} , the modeling captures the transition to a first-order approximation. For a cooling rate of 2 Ks^{-1} , however, it was found from the measured data at smaller cooling rates and modeling that the measured data are suspect. Nevertheless, although it was concluded that their model oversimplifies the physics, they did not cast doubt. A different approach was followed by Fleischmann and Koppelman³ who noticed that the specific volume for semicrystalline polymers below the melting point increases with increasing cooling rates. This results from a suppressed crystallization process as low temperatures are reached fast. To get a grip on the phenomenon, a specific volume corrected for high pressures and high cooling rates was calculated, instead of using a calculated crystal structure distribution to determine the specific volume.

In summary, problems with standard pVT measurements on semicrystalline polymers are

- In both the isothermal and isobaric modes, when using an increasing temperature run, the initial crystal structure of the sample is not known. The reference point for such an experiment is absent.
- In both the isothermal and isobaric modes, when using a decreasing temperature run, the cooling rate influences the crystal struc-

ture and the resulting specific volume. Moreover, a steady state in the material is assumed, while crystalline structures are continuously changing the specific volume. Specific volume measurements show only a moment in time of the processes during these measurements.

- In both an increasing and decreasing temperature run, when using the isothermal mode, pressure enhanced nucleation/(re)crystallization can occur. This means that all measured points at a particular pressure are influenced by the other pressures in the cycle. The material in the accompanying pressure measurements possibly has a different crystalline structure and, as a result, a different specific volume.
- Since high cooling rates cannot be reached in standard techniques, the results of these measurements are inadequate for injection-molding simulations.

A different experimental setup to measure the specific volume of semicrystalline polymers could solve these problems. Since the cooling rate influences the crystal structure, measurements at different cooling rates are necessary; however, temperature gradients in the sample have to be prevented. Therefore, a setup based on the confining fluid technique was developed that can reach cooling rates of the sample up to 60 Ks^{-1} and pressures up to $20 \times 10^6 \text{ Pa}$. During an experiment, the specific volume and temperature history of the thin sample are registered together with the pressure applied. Sample thickness is such that temperature gradients in the sample are negligibly small. The time-temperature development in the sample, an accurate model for the crystallization kinetics, and a crystallinity-dependent model for the specific volume, and combining all these three aspects, result in accurate predictions of the specific volume. Measurement and simulation results can be compared to determine model parameters.

EXPERIMENTAL

Methods

When using the confining fluid technique, the basic experiment is the following:

- Include the sample in the fluid cell,

- Fill the cell with the confining fluid,
- Build up the required pressure level,
- Heat the cell to the required starting temperature,
- Cool the sample.

Since in the injection-molding process high pressures can be present, the experimental setup has to be able to reach these values also to generate useful data. For this reason, pressures have to be reached up to $p = 1 \times 10^8 \text{ Pa}$. Temperatures should be able to reach $T = 623 \text{ K}$ to cover the melting temperatures of several polymers, while cooling rates should be as high as possible. Two experimental runs are necessary: one with the sample and one without the sample as a baseline for setup influences.

While cooling rates are high, the thickness of the sample should be as small as possible to minimize temperature gradients in the sample. A manageable maximum thickness of $\leq 0.35 \text{ mm}$ was chosen. Samples with a length of approximately 30 mm and a width of approximately 18 mm were formed by compression molding pellets at a temperature $T = 500 \text{ K}$ at low pressures. Sample cooling was done at atmospheric pressure. Measurement of the experimental temperature takes place at six different positions at the cavity surface (T_{Lb}, \dots, T_{Ro}), while the pressure is measured at the top and the bottom of the cavity (P_b, P_o). The volume difference is registered using an LDVT displacement transducer (D) mounted to the bellows bottom (Fig. 1). To minimize the influence of heat on the rest of the measuring equipment, cooling channels are present at the top and the bottom of the heated area to create heat sinks (Fig. 2). When steady conditions are reached, the vicinity of the sample is quenched with pressurized water via cooling channels positioned close to the sample holding area (Fig. 2). During cooling, the temperature history, pressure, and volume difference are measured at a frequency of $50\text{--}100 \text{ Hz}$, dependent on the cooling applied. Notice that the cooling rate is never constant but is determined by the flux and temperature of the coolant in combination with the heat capacity of the sample-holding area. Since the flux is kept constant and the cooling rate thus varies, the actual temperature history will be used in analyzing the experimental results. The maximum in the time derivative of the temperature (\dot{T}_{max}) is called the cooling rate. The maximum cooling rate achieved is 54.2 Ks^{-1} (Fig.

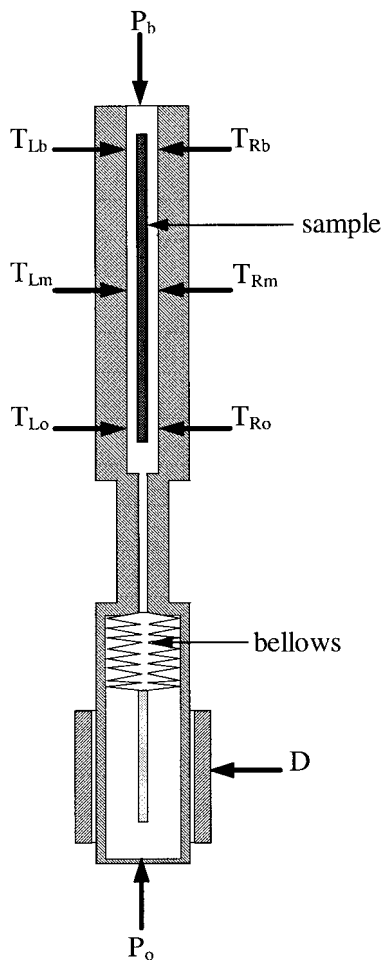


Figure 1 Basic outline of the setup.

3). The maximum pressure achieved up to now, without any experimental problem, was $p = 177 \times 10^5$ Pa. The specific volume is obtained by relating the volume difference to the specific volume of the polymer melt at the starting temperature, measured using standard pVT measurements (Moldflow⁸).

Modeling the degree of crystallinity ξ is done using Schneider's rate equations (Schneider et al.²⁰). They fully characterized the structure, that is, mean number of spherulites and their radius, surface, and volume. These equations consist of a series of nested differential equations:

$$\begin{aligned}
 \dot{\phi}_3 &= 8\pi\alpha & (\phi_3 &= 8\pi N) \\
 \dot{\phi}_2 &= G\phi_3 & (\phi_2 &= 4\pi R_{\text{tot}}) \\
 \dot{\phi}_1 &= G\phi_2 & (\phi_1 &= S_{\text{tot}}) \\
 \dot{\phi}_0 &= G\phi_1 & (\phi_0 &= V_{\text{tot}})
 \end{aligned} \tag{1}$$

in which ϕ_0 is the undisturbed total volume V_{tot} of the spherulites per unit of volume; ϕ_1 , the total surface S_{tot} of the spherulites per unit of volume; ϕ_2 , 4π times the sum of the radii R_{tot} of the spherulites per unit of volume; and ϕ_3 , 8π times the number of the spherulites N per unit of volume (if impingement and swallowing are disregarded, meaning that the nucleation rate α does not depend on the volume fraction of already crystallized material). The crystal growth rate G and the nucleation rate α have to be measured as a function of temperature. These rate equations are based on the generalized Kolmogoroff equation (Janeschitz-Kriegl²¹), in which the nucleation is random in time and spatially uniform. Crystal impingement is described using the Avrami model¹:

$$-\ln(1 - \xi_g) = \phi_0 \tag{2}$$

in which ξ_g is the degree of space filling. The degree of crystallinity ξ can be obtained by multiplying the degree of space filling with the local degree of crystallinity V_∞ in each spherulite. This set of equations [eqs. (1) and (2)] fully characterizes the spherulitical structure development during an experimental run and the structure present in the sample is known all the time. When the degree of space filling ξ_g does not reach unity during an experimental run, the remaining portion of the material is assumed to be in a mesomorphic phase. This results, at high cooling rates, in a material consisting of spherulites in a mesomorphic matrix.

Since the specific volume ν of a semicrystalline polymer is always a combination of the amorphous and crystalline structure present, it is assumed that both phases are not influenced by each other. A crystallinity-dependent model for the specific volume distinguishes between the amorphous ρ_a^* and the crystalline contribution ρ_c^* to the density ($\rho = 1/\nu$) using the volume fraction of the crystallized material $\xi_g V_\infty$, without mutual influences:

$$\rho = \xi_g V_\infty \rho_c^* + (1 - \xi_g V_\infty) \rho_a^* \tag{3}$$

Since the Tait equation does not yield a good representation of the compressibility behavior of solid semicrystalline polymers (Zoller¹⁶), and the transition from melt to solid by crystallization is not a transition explicitly, it is not clear when the Tait equation can be used. Therefore, both the

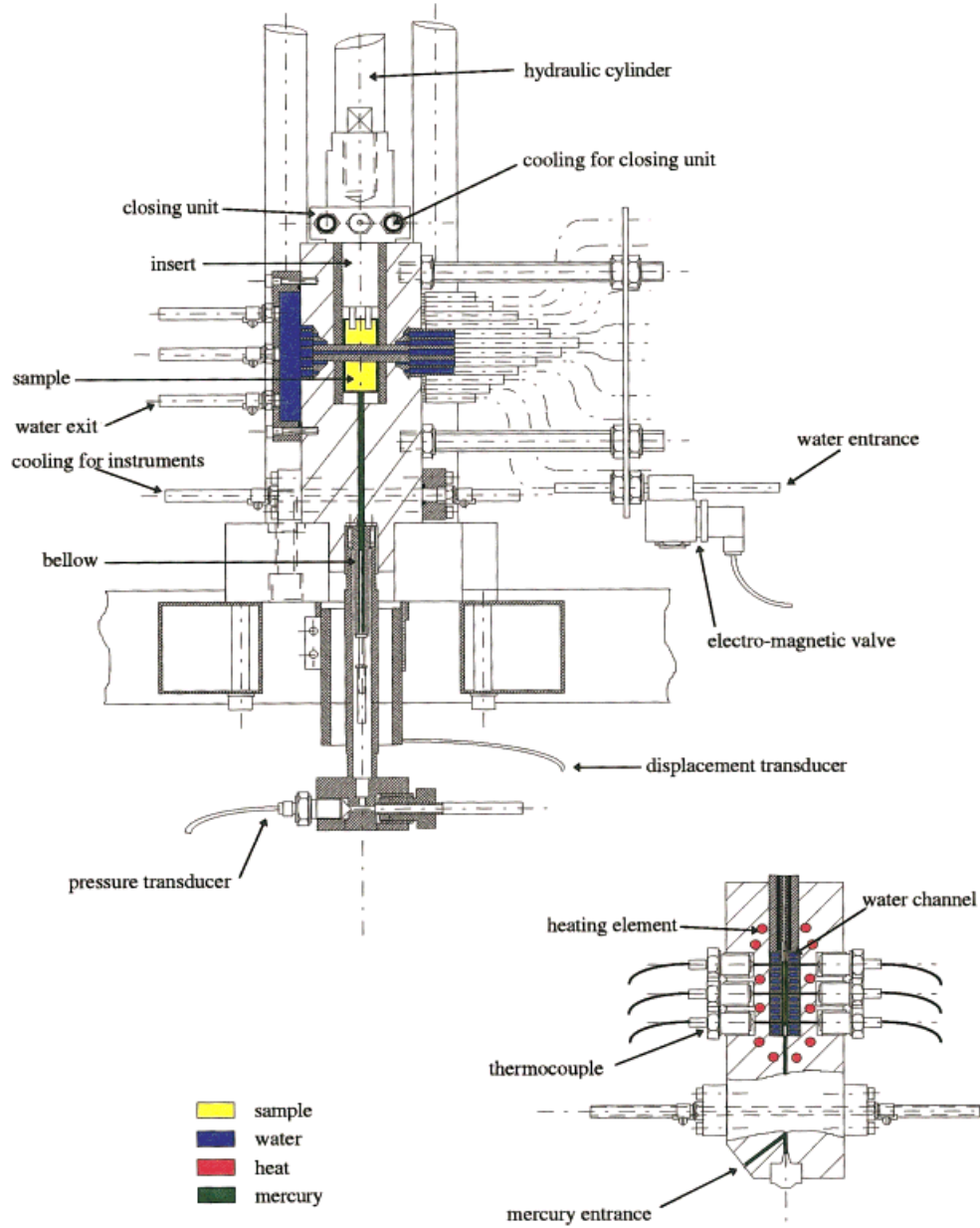


Figure 2 Detailed outline of the setup.

amorphous ρ_a^* and the crystalline contribution ρ_c^* are modeled using a Taylor series in temperature and pressure:

$$\Delta T = T - T_{\text{ref}} \quad (4)$$

$$\Delta p = p - p_{\text{ref}} \quad (5)$$

$$\rho_i^* = \rho_{\text{ref},i} + \frac{\partial \rho_i}{\partial T} \Delta T + \frac{\partial \rho_i}{\partial p} \Delta p + \frac{\partial^2 \rho_i}{\partial T \partial p} \Delta T \Delta p + \frac{\partial^2 \rho_i}{\partial T^2} \Delta T^2 + \frac{\partial^2 \rho_i}{\partial p^2} \Delta p^2 \quad i = a, c \quad (6)$$

Materials

The material investigated is an isotactic polypropylene (K2Xmod, Borealis). This C3-homopolymer with high stereoregularity and heterogeneous nucleation is a high-stiffness grade for injection-molding and cast-film applications. Molecular data were obtained by Borealis Austria using GPC (TCB/408 K/mixed-bed column, PS calibration) and are shown in Table I. Standard pVT measurements were performed by Moldflow⁸ using a GNOMIX RESEARCH confining fluid pVT apparatus in the isothermal mode starting at

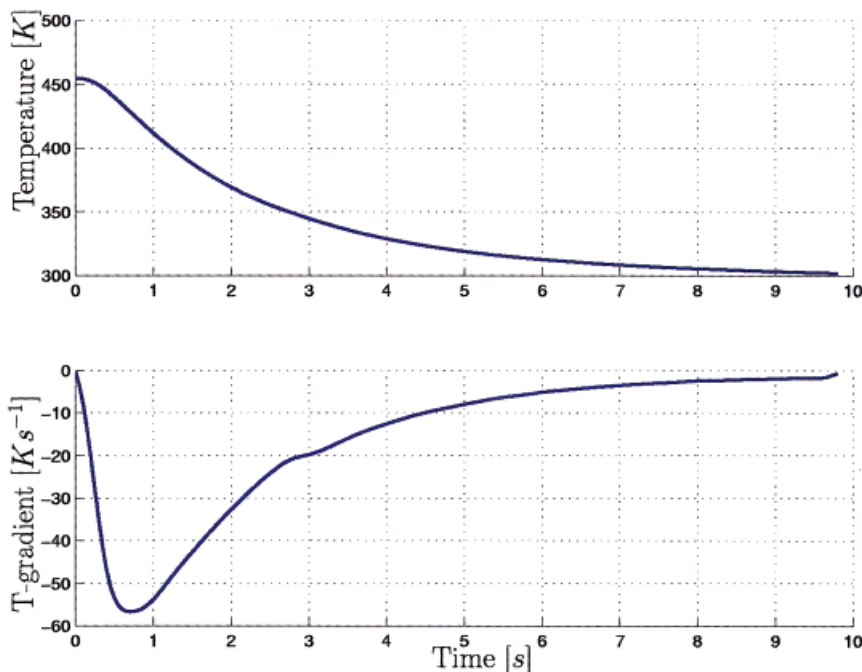


Figure 3 (Top) Measured temperature signal in time together with (bottom) the calculated time derivative in time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the ambient temperature (heating cycle) over a 10–160 MPa pressure range (Fig. 4). From these measurements, the parameters were determined (Table IV), which describe the lower- and higher-temperature asymptotes using the specific volume model. The number of spherulites as a function of temperature was determined by Linz University (Austria), using a quenching technique, and is described by

$$N = n_1 T + n_2, \quad T \leq T_m \quad (7)$$

for which the parameters are given in Table III (Fig. 5). The crystal growth rate as a function of temperature was determined by Linz University (Austria), using thin-film crystallization and is described by

$$G = G_{\max} e^{-2 \frac{[T - T_{\text{ref}} - \alpha(p - p_{\text{ref}})]^2}{\beta}} \quad (8)$$

Table I Molecular Data of the Isotactic Polypropylene (K2Xmod, Borealis) Obtained Using GPC

M_w	365 kg mol ⁻¹
M_n	67 kg mol ⁻¹

for which the parameters are given in Table III (Fig. 6).

RESULTS AND DISCUSSION

The temperature and specific volume measured during an experimental run in the isobaric mode at $p = 1 \times 10^5$ Pa are shown in Figure 7. The effect of the crystallization on the specific volume of the sample becomes noticeable around approximately $t = 3$ s after the start of the cooling (Fig. 7, bottom). By using the time–temperature measurement as a boundary condition, predictions on the degree of crystallinity can be made using Schneider's rate equations and Avrami's model of impingement. The specific volume can be calculated using the proposed formulation [eqs. (3)–(6)] and the parameters shown in Table IV.

Table II Model Parameters for the Number of Crystals of the Isotactic Polypropylene (K2Xmod, Borealis) Using Eq. (7)

n_1	$-2.6087 \times 10^{13} \text{ K}^{-1}$
n_2	$6.5783 \times 10^{15} \text{ K}^{-1}$

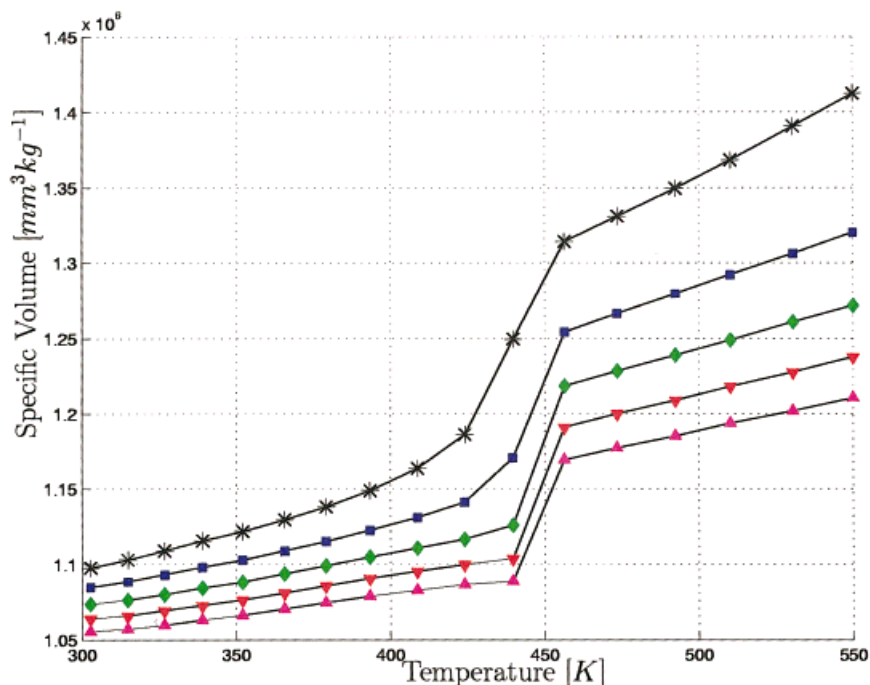


Figure 4 Standard pVT data of the iPP K2Xmod at pressures of (*) 0.1, (■) 40, (◆) 80, (▽) 120, and (△) 160 MPa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Comparison between the measured and the predicted specific volume is shown in Figure 8, together with the measured specific volume according to the standard procedure (Moldflow⁸). The most striking agreement between the measured and calculated specific volume is the temperature of the crystallization transition. The position of this transition depends on the crystal-growth rate and the number of crystals present, which are both a function of the (local) temperature. A deviation in the measured temperature, which is used as a boundary condition for the simulations, will cause a difference in the position of this transition. Consequently, the modeling of the crystallization kinetics is in accordance with the physical phenomena measured. The main dif-

ference between the standard data and the measured specific volume is due to the influence of the procedure used. The standard data (Moldflow⁸) are measured using an increasing temperature run, which results in a melting transition around approximately $T = 430$ K. The new measurements are performed using a decreasing temperature run, which results in a crystallization transition around $T = 370$ K.

The difference between these measurements, therefore, consists of the influence of the cooling rate on the crystallization kinetics (studied in the next subsection) together with a different physical phenomenon: melting versus crystallization. The latter can be observed in DSC runs as well. A similar difference in the transition temperature for the melting and crystallization of polypropylene was observed by He and Zoller.⁴ Moreover, from Fleischmann and Koppelman,³ Hieber,¹⁹ Zoller,¹⁶ and others, it is known that the crystalline phase has a much smaller temperature and pressure sensitivity than that of the amorphous phase. Our results are not in contradiction with this.

While the Schneider rate equations do not only describe the resulting degree of crystallinity, but

Table III Model Parameters for the Crystal-growth Rate of the Isotactic Polypropylene (K2Xmod, Borealis) Using Eq. (8)

G_{\max}	$8.1 \times 10^{-6} \text{ ms}^{-1}$
T_{ref}	$83.8 \text{ }^{\circ}\text{C}$
β	$1126.9 \text{ }^{\circ}\text{C}^2$
a	$5 \times 10^{-7} \text{ KPa}^{-1}$
p_{ref}	$1 \times 10^5 \text{ Pa}$

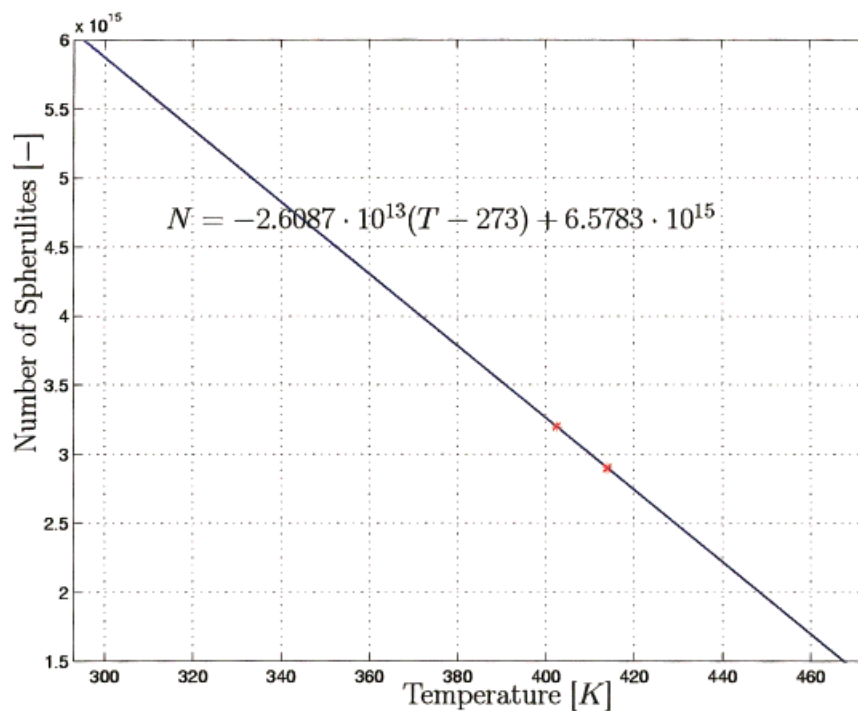


Figure 5 (*) Measurements and (—) fit on the number of spherulites of the iPP K2Xmod. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

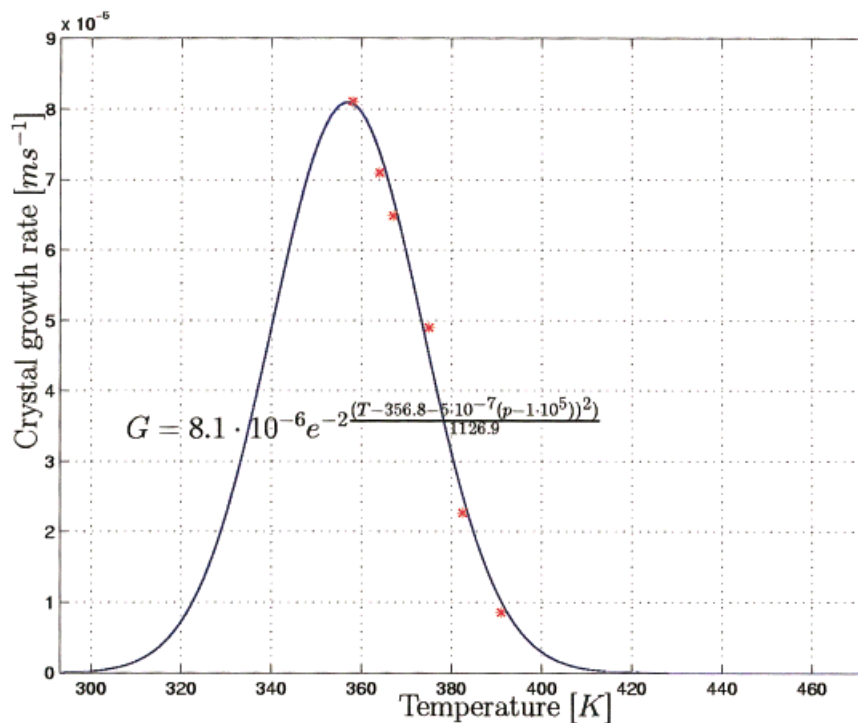


Figure 6 (*) Measurements and (—) fit on the crystal-growth rate of the iPP K2Xmod at atmospheric pressure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

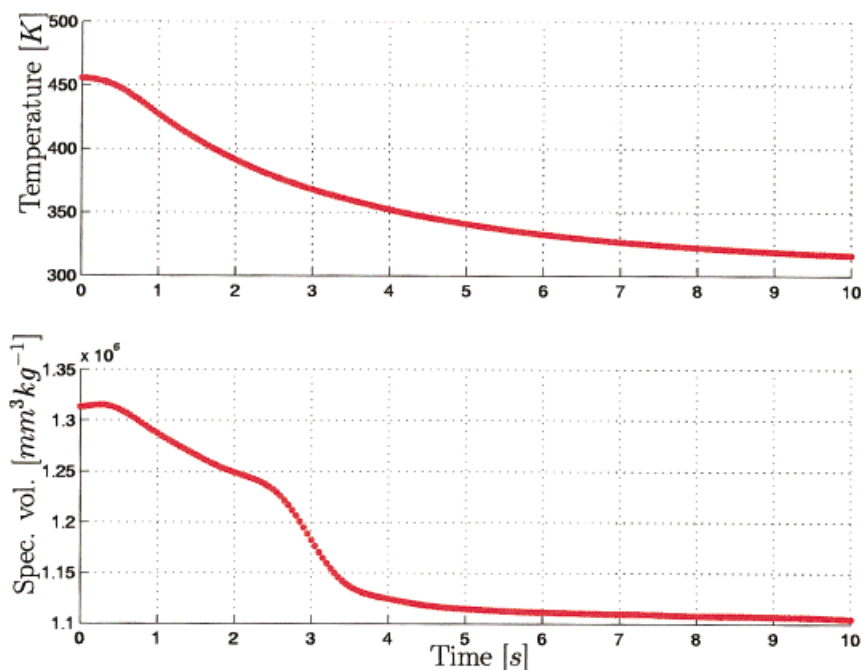


Figure 7 (Top) Measured temperature signal in time together with (bottom) the measured specific volume signal in time during an experimental run in the isobaric mode at $p = 1 \times 10^5$ Pa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

also give a full description of the average properties of the resulting structure, it is possible to reproduce the structure development during crystallization by generating (at random) nuclei with an average rate equal to the local nucleation rate. For different times during crystallization, the distribution of the structure over the thickness of the

Table IV Model Parameters for the Specific Volume, Using Eq. (6)

T_{ref}	273 K
p_{ref}	1×10^5 Pa
V_{∞}	0.80
ρ_a	8.7796×10^{-7} kg mm $^{-3}$
$(\partial \rho_a)/(\partial T)$	-6.40×10^{-10} kg mm $^{-3}$ K $^{-1}$
$(\partial \rho_a)/(\partial p)$	6.0×10^{-16} kg mm $^{-3}$ Pa $^{-1}$
$(\partial^2 \rho_a)/(\partial T^2)$	0.0 kg mm $^{-3}$ K $^{-2}$
$(\partial^2 \rho_a)/(\partial p \partial T)$	2.10×10^{-18} kg mm $^{-3}$ K $^{-1}$ Pa $^{-1}$
$(\partial^2 \rho_a)/(\partial p^2)$	-2.6×10^{-24} kg mm $^{-3}$ Pa $^{-2}$
ρ_c	9.3896×10^{-7} kg mm $^{-3}$
$(\partial \rho_c)/(\partial T)$	-4.24×10^{-10} kg mm $^{-3}$ K $^{-1}$
$(\partial \rho_c)/(\partial p)$	2.0×10^{-16} kg mm $^{-3}$ Pa $^{-1}$
$(\partial^2 \rho_c)/(\partial T^2)$	0.0 kg mm $^{-3}$ K $^{-2}$
$(\partial^2 \rho_c)/(\partial p \partial T)$	1.30×10^{-18} kg mm $^{-3}$ K $^{-1}$ Pa $^{-1}$
$(\partial^2 \rho_c)/(\partial p^2)$	0.0 kg mm $^{-3}$ Pa $^{-2}$

sample is shown (Fig. 9, left side), where the upper parts show the spherulitical structure. The lower parts give the local degree of crystallinity (solid), calculated by counting pixels in the upper part. When different crystals capture the same pixel by growth, this is registered as an interface. Moreover, the resulting structure in the sample can be compared easily by transforming the reproduction of the structure (Fig. 9, left side) to the same structure when viewed using polarized light under a microscope (Fig. 9, right side). The resulting main spherulite radius is approximately 7 μm , which is smaller than is the 25 μm measured by Piccarolo¹⁴ under similar experimental conditions. However, as nucleation density in a material has a large influence on this, the different polypropylenes used are probably the reason for this discrepancy.

Influence of Cooling Rate

Different cooling rates were applied ($\dot{T}_{\text{max}} = 0.21, 33.96, 44.58, \text{ and } 54.22$ Ks $^{-1}$). In Figure 10, the measured specific volume is shown together with the calculated one using the procedure described in the previous subsection. The shift in the crys-

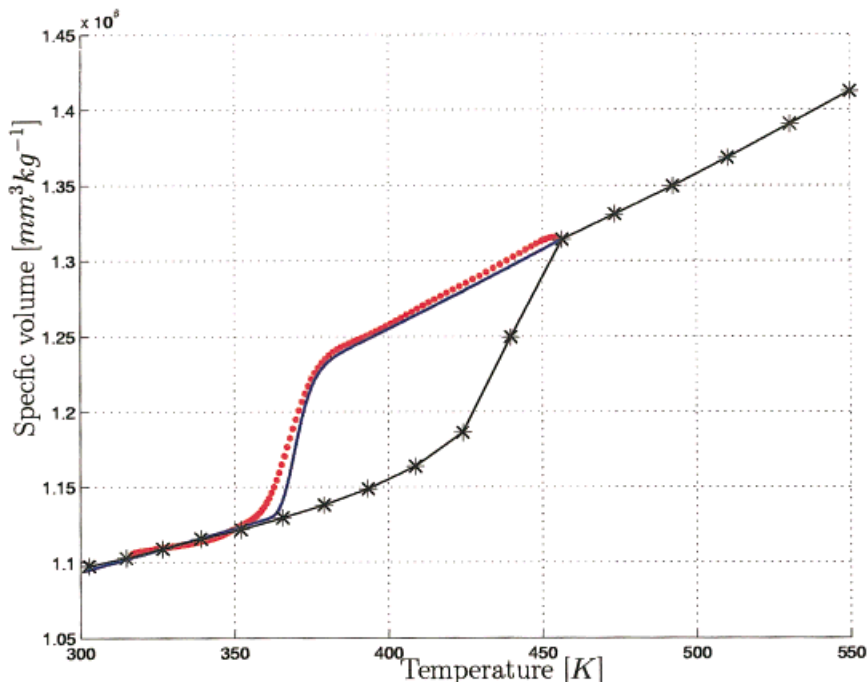


Figure 8 (—) Calculated and (●) measured (cooling cycle) specific volume as a function of the measured temperature (see Fig. 7, top) together with (*), the measured (heating cycle) specific volume according to the standard procedure (Moldflow⁸). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tallization transition, due to the different crystallization kinetics in the sample, is approximately 50 K from a cooling rate of $\dot{T}_{\max} = 0.21$ to 54.22 Ks^{-1} . At a low cooling rate ($\dot{T}_{\max} = 0.21 \text{ Ks}^{-1}$), the residence time at higher temperatures enables the growth of fewer crystals at low rates. In contrast, at a high cooling rate ($\dot{T}_{\max} = 54.22 \text{ Ks}^{-1}$), the residence time at higher temperatures is so low that the degree of crystallinity hardly increases in that range. However, as cooling progresses to lower temperatures, the number of crystals and their crystal growth rate increases (see Figs. 5 and 6, respectively) and so will the degree of crystallinity. As a result, the transition in the specific volume shifts to lower temperatures.

In the utmost case where the cooling rate is so high that the degree of crystallinity is still minor at very low temperatures ($T = 293 \dots 353 \text{ K}$), the crystal-growth rate decreases with decreasing temperatures due to the lower molecular mobility at these temperatures (Fig. 6). Consequently, the degree of crystallinity will not reach the maximum value and the crystallization transition will be at a very low temperature and be less pronounced. The resulting structure then will consist

of spherulites in a mesomorphic matrix as discussed in the Experimental section.

The agreement between the measured and the calculated specific volume is rather good at low cooling rates, while at high cooling rates, there is a little difference. This might be caused by a different crystal structure at these cooling rates, which has a different crystal growth rate distribution. This is in accordance with the work of Piccarolo,²² who stated that, at high undercoolings, the mesomorphic phase forms faster and with a high degree of disorder, while at low undercoolings, the mobility allows high growth rates to be obtained with the gain of a well-ordered α -monoclinic structure. For the low cooling-rate experiment ($\dot{T}_{\max} = 0.21 \text{ Ks}^{-1}$), the crystallization transition temperature is around $T \approx 407 \text{ K}$, which is comparable with the value found by Ito et al.,²³ $T \approx 398 \text{ K}$, at a cooling rate of $\dot{T} = 0.0167 \text{ Ks}^{-1}$ and atmospheric pressure.

Influence of Pressure

Different pressures are applied to study the influence of the pressure on the crystallization kinet-

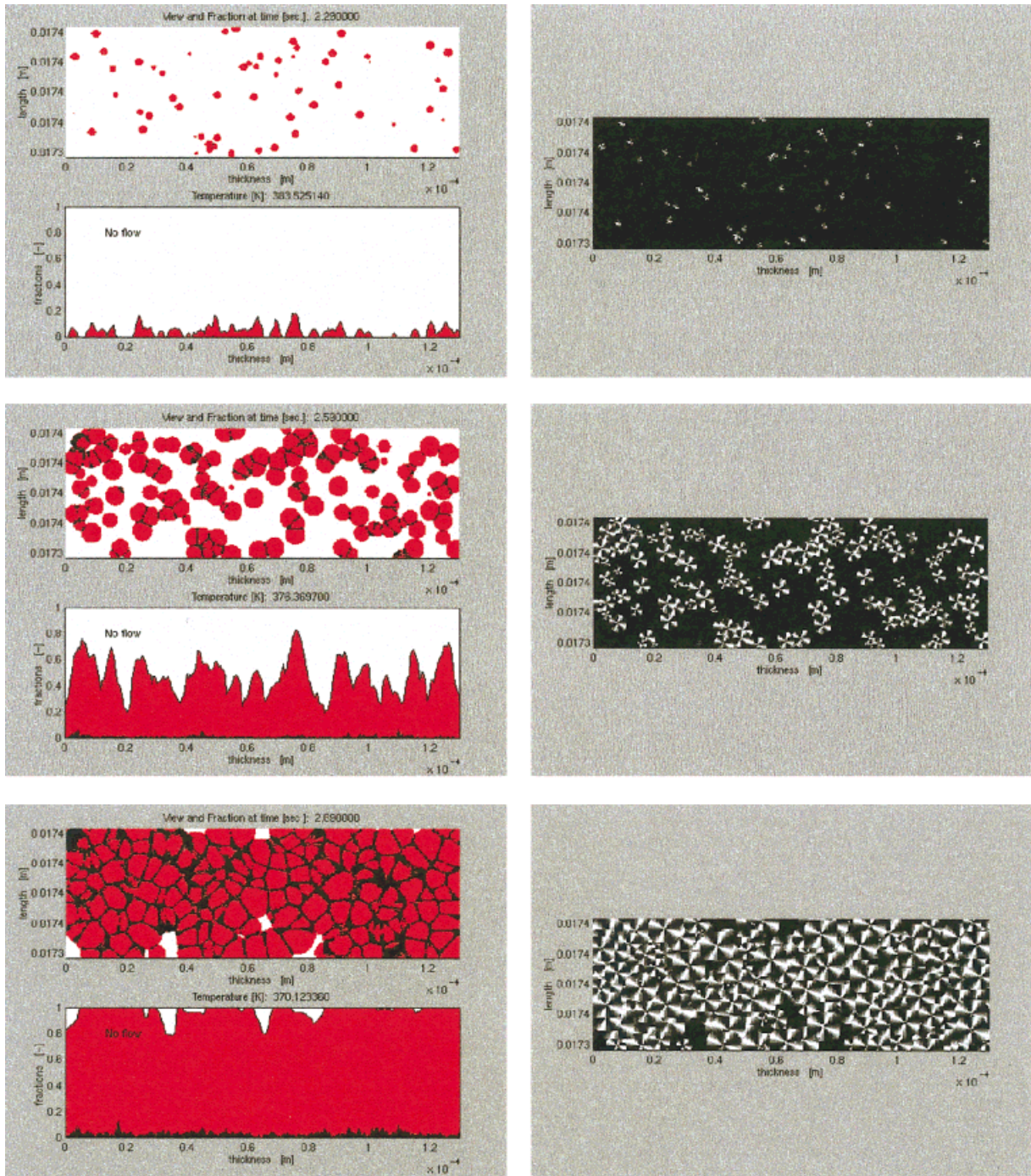


Figure 9 (Left side) Computed reproduction of the structure using Schneider's rate equations from the center of the sample (thickness = 0 m) to the surface (thickness = 0.00013 m) for (upper parts) different moments during crystallization, together with (lower parts) an impression of the local degree of crystallinity. (Right side) Visualization of the structure from the center of the sample to the surface when viewed using polarized light microscopy.

ics. The cooling rate applied in these experiments was around $\dot{T}_{\max} = 40 \text{ Ks}^{-1}$ (Table V). In Figure 11, the measured specific volume is presented for

all pressures. Besides a normal shift to a lower specific volume at a higher pressure, an extra shift in the crystallization transition temperature

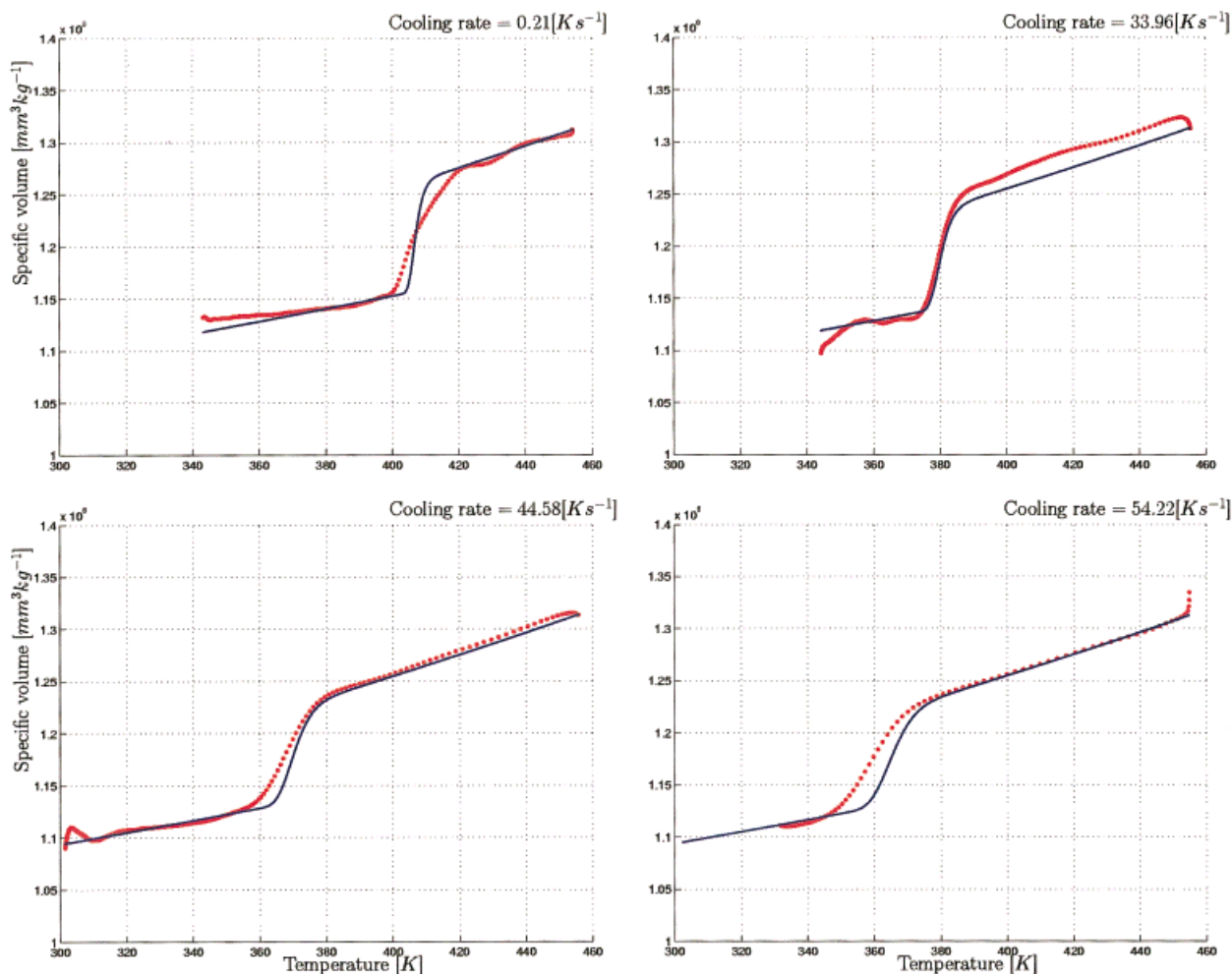


Figure 10 (—) Calculated and (●) measured specific volume as a function of the measured temperature for different cooling rates ($\dot{T}_{\max} = 0.21, 33.96, 44.58, \text{ and } 54.22 \text{ K s}^{-1}$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

is present. This is caused by the shift in the crystal growth rate distribution to higher temperatures at an increasing pressure.

Table V Different Pressures Applied to Study the Influence of the Pressure on the Crystallization Kinetics Together with the Experimentally Observed Cooling Rate

p (Pa)	\dot{T}_{\max} (Ks ⁻¹)
3×10^5	40.24
26×10^5	40.74
101×10^5	37.40
177×10^5	39.71

For a polypropylene, it was shown by Ito et al.,¹⁰ that the melting and glass transition temperatures depend linearly on pressure with a proportionality factor $a = 3 \times 10^{-7} \text{ KPa}^{-1}$. He and Zoller⁴ found this factor to be $a = 2.899 \times 10^{-7} \text{ KPa}^{-1}$ for the melting temperature and $a = 2.287 \times 10^{-7} \text{ KPa}^{-1}$ for the glass transition temperature, while Leute et al.²⁴ determined $a = 3.8 \times 10^{-7} \text{ KPa}^{-1}$ independent of the molecular weight. If the transition temperatures depend on pressure in a linear way, one can assume that the crystal growth rate curve, which is related to these, is shifted in the same way. Therefore, the crystal growth rate distribution is shifted to higher temperatures with increasing pressure without changing the shape [eq. (8), Fig.

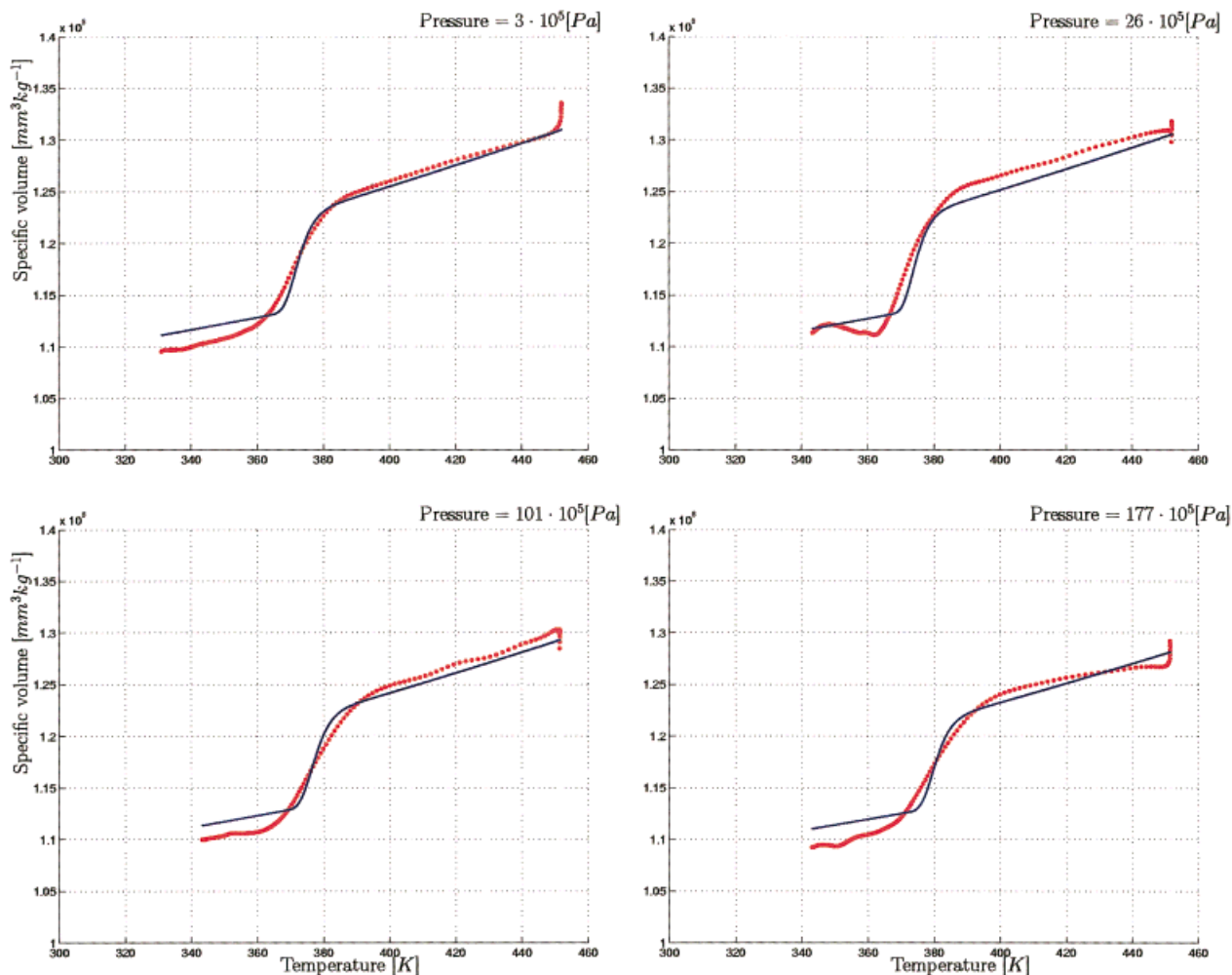


Figure 11 (—) Calculated and (●) measured specific volume as a function of the measured temperature for different pressures ($p = 3 \times 10^5$, 26×10^5 , 101×10^5 , and 177×10^5 Pa) at a cooling rate around $\dot{T}_{\max} = 39.52 \text{ Ks}^{-1}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

6]. Using the factor $\alpha = 5 \times 10^{-7} \text{ KPa}^{-1}$ (Table III), fitted using the measurements (Fig. 11), the calculation of the crystal structure (specific volume) is made dependent on the pressure. The results are presented in Figure 11 as well. The factor α used is somewhat larger than are the values mentioned previously, but is of the same order. This small difference can be due to material characteristics (nucleation and crystal growth rate distribution). It can be concluded, accordingly, that the crystallinity-dependent model for the specific volume is able to describe the phenomena observed during the experiments. Moreover, modeling the crystallization process accurately results in accurate predictions for the specific volume.

Influence of Cooling Rate and Pressure

Using the results from the experiments described above, a numerical study for higher cooling rates and higher pressures can be performed to demonstrate the behavior of the modeling in this range. Of course, these results should be considered with some reservation, as they are extrapolations. The specific volume is calculated for a range of pressures ($p = 0.1, 40, 80, 120$, and 160 MPa) and different temperature histories. A starting temperature $T_{\text{start}} = 550 \text{ K}$ and an end temperature $T_{\text{end}} = 300 \text{ K}$ were applied together with a range of constant cooling rates $\dot{T} = 0.017, 40, 80$, and 120 Ks^{-1} . At a very low cooling rate of $\dot{T} = 0.017 \text{ Ks}^{-1}$, the calculated specific volume (Fig. 12, top

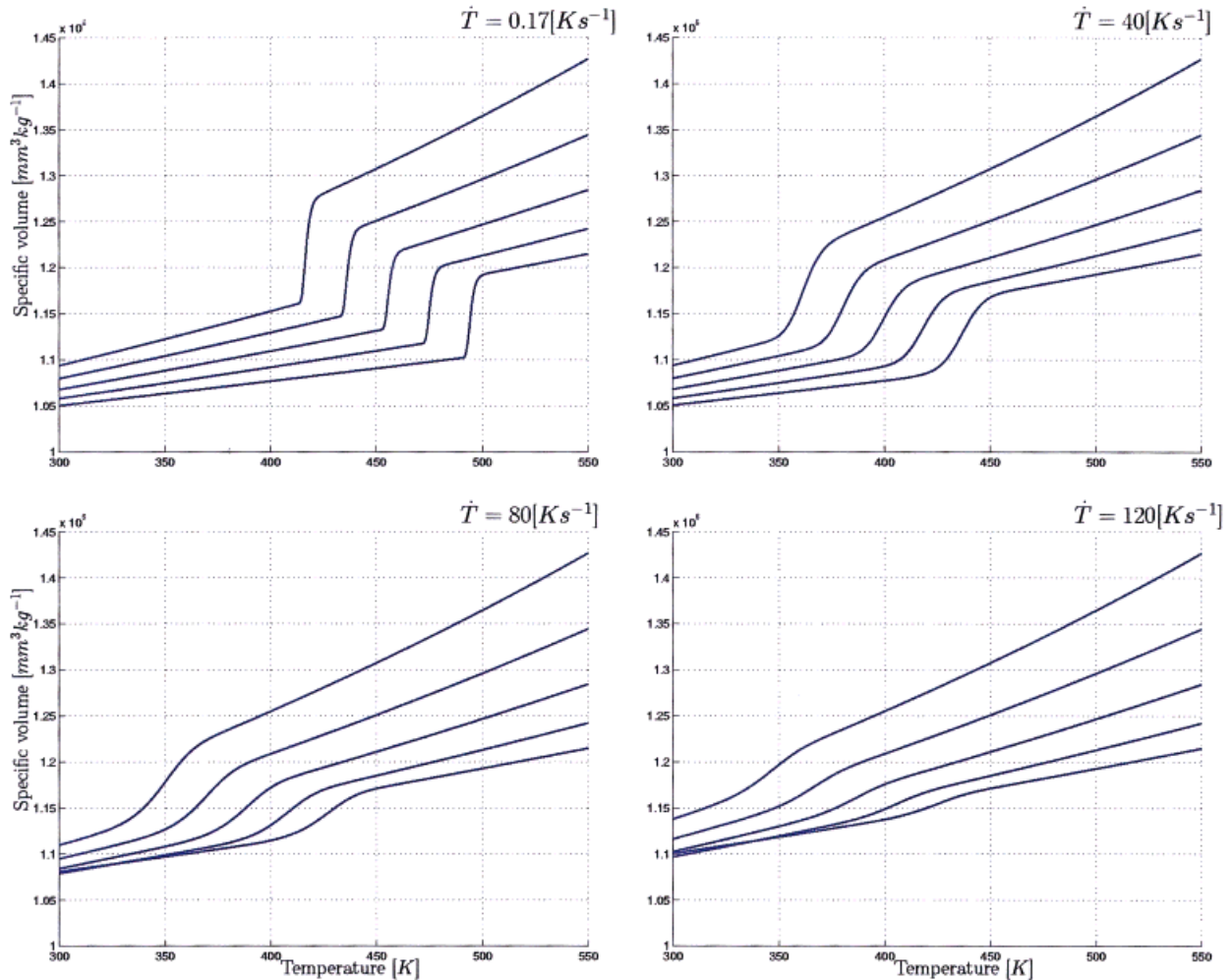


Figure 12 (—) Calculated specific volume for a cooling rate (top left) $\dot{T} = 0.017$, (top right) 40, (bottom left) 80, and (bottom right) 120 Ks^{-1} . The pressures applied are $p = 0.1, 40, 80, 120,$ and 160 MPa . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

left) matches the experiments done by Moldflow (Fig. 4). The temperature of the crystallization transition differs from the melting transition in the Moldflow data as discussed previously. When the cooling rate is increased to $\dot{T} = 40 \text{ Ks}^{-1}$ (Fig. 12, top right), the crystallization transition is shifted to lower temperatures, although the resulting specific volume at the end temperature remains the same. However, when cooling is increased to $\dot{T} = 80 \text{ Ks}^{-1}$ (Fig. 12, bottom left), the residence time at a temperature which enables crystal growth is so low that the material does not crystallize fully. As a result, the specific volume at the end temperature is higher, because not all material has crystallized in the spherulite form, but a mesomorphic phase is partly present.

Since no information is available on the change of the distribution of the number of crystals with increasing pressure, it is assumed that this distribution stays unchanged. Moreover, it has been shown that increasing the pressure does not fundamentally alter mechanisms of nucleation (He and Zoller⁴). Consequently, the final degree of crystallinity of the sample will be less at higher pressures. The crossover in Figure 12 (bottom left) from a pressure of $p = 120$ to 160 MPa is a result of this. Experimental verification of the number of crystals at different pressures has to be done to confirm this. Increasing the cooling rate to $\dot{T} = 120 \text{ Ks}^{-1}$ shows the same effect but more pronounced (Fig. 12, bottom right).

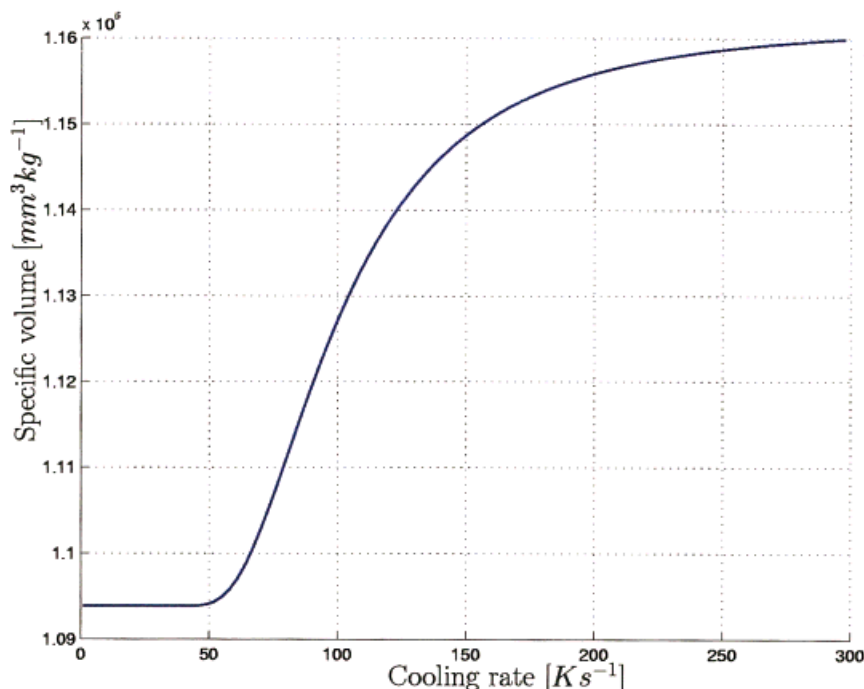


Figure 13 Calculated specific volume for cooling rates up to $\dot{T} = 300 \text{ K s}^{-1}$ for the isotactic polypropylene (K2Xmod). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Observations by Piccarolo¹⁴ made clear that increasing the cooling rate from $\dot{T} \approx 0 \text{ K s}^{-1}$ to $\dot{T} = 311 \text{ K s}^{-1}$ results in a transition from a mainly spherulitical structure to a mainly mesomorphic structure. The model enables us to calculate such a transition (Fig. 13). Using the same temperature history as described above, the cooling rate is varied from $\dot{T} \approx 0 \text{ K s}^{-1}$ to $\dot{T} = 300 \text{ K s}^{-1}$. The transition is present around $\dot{T} \approx 50 \leftrightarrow 250 \text{ K s}^{-1}$, while the measurements of Piccarolo¹⁴ showed this transition at $\dot{T} \approx 20 \leftrightarrow 80 \text{ K s}^{-1}$. The difference probably is caused by the different material characteristics (nuclei and crystal growth rate distribution) of the isotactic polypropylenes used.

CONCLUSIONS

When using standard pVT measurements on semicrystalline polymers, problems range from the absence of uniform hydrostatic pressures (piston-die technique) and low cooling rates (piston-die and confining fluid technique) to an unknown specific volume distribution during cooling (Piccarolo's quenching technique), as expressed in the Introduction. Therefore, a setup based on the confining fluid technique was developed that can

reach cooling rates of the sample up to 60 K s^{-1} and pressures up to $20 \times 10^6 \text{ Pa}$. In this way, the specific volume can be measured during cooling at cooling rates comparable with the ones present during the injection-molding process. Comparing measurements using the confining fluid technique in an increasing temperature run, with measurements using the new setup in the isobaric mode, show the influence of the procedure used on the specific volume of a semicrystalline polymer. The confining fluid technique results in a melting transition around approximately $T = 430 \text{ K}$, while measurements with the new setup show a crystallization transition around $T = 370 \text{ K}$. This difference consists of the influence of the cooling rate on the crystallization kinetics together with the difference between melting and crystallization, also known from DSC experiments. The influence of the pressure on the crystal growth rate distribution is determined by measuring the specific volume at a constant cooling rate at pressures up to $p = 177 \times 10^5 \text{ Pa}$. Besides a normal shift to a lower specific volume at a higher pressure, an extra shift in the crystallization transition temperature is present. Modeling the specific volume is done by combining a set of equations that fully describe the crystal

structure during an experimental run, with a Taylor series in pressure and temperature. This combination accurately describes the specific volume measured at cooling rates of $\dot{T} = 0.21$ and 33.96 Ks^{-1} , while at cooling rates of $\dot{T} = 44.58$ and 54.22 Ks^{-1} , there is a little difference. This difference might be caused by a different crystal structure at these cooling rates, which results in a different crystal growth rate distribution.

In conclusion, the new setup enables measurements of the specific volume at injection-molding conditions. Moreover, results at low cooling rates are in accordance with results presented by Ito et al.,²³ Moldflow,⁸ and Zoller¹⁶; results at elevated pressures are in accordance with results presented by He and Zoller,⁴ Ito et al.,¹⁰ and Leute et al.²⁴; and results at high cooling rates show a resemblance to the work of Piccarolo.¹⁴ The results, moreover, stress that standard techniques are not able to characterize the specific volume of semicrystalline polymers. Therefore, crystallization kinetics in the sample have to be known to obtain detailed information on the specific volume for semicrystalline polymers. An experimental-numerical approach seems inevitable. On the one hand, modeling the crystallization process accurately results in accurate predictions for the specific volume. On the other hand, measuring the specific volume at a range of cooling rates and pressures gives a first impression of the crystallization kinetics in the material. These experiments will be extended to higher pressures and cooling rates, while the influence of flow will be studied by using different kind of experiments (Swartjes et al.²⁵) and modeling (Zuidema et al.¹).

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