Thermochimica Acta, 238 (1994) 397–415
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01582-N

Pressure–volume–temperature studies of semi-crystalline polymers

Paul Zoller * and Youssef A. Fakhreddine
University of Colorado, Department of Mechanical Engineering, Boulder, CO 80309 (USA)

(Received 25 January 1993; accepted 25 October 1993)

Abstract

The applications of pressure–volume–temperature (*PVT*) techniques to the study of semi-crystalline polymers are surveyed. The principles of the two major experimental techniques, the piston-die dilatometer and the confining fluid apparatus, are compared and critiqued. Data obtained on a confining-fluid-type *PVT* apparatus are used to illustrate the measurement of the equations of state (and derived properties) of melts and solids, the pressure dependence of melting points and crystallization temperatures, the process of annealing in the solid state, and the study of the crystallization kinetics of polymers.

INTRODUCTION

The measurement of the specific volume of a material as a function of pressure and temperature (*PVT* measurement or pressure dilatometry) is a powerful physical characterization tool in many areas of materials science. The measured quantity, the specific volume, reflects accurately the state and the changes of state of materials.

In polymer physics and polymer engineering, *PVT* measurements have developed from a laboratory speciality to a fairly widely practiced physical characterization technique, in part due to the development of reliable and relatively simple-to-use commercial equipment. *PVT* measurements have become the technique of choice to characterize the thermophysical behavior of polymers and other materials at pressures to 200 MPa (or 2000 bar). It is important to include pressure in studies of polymers because their behavior is sensitive to pressure, and because polymers are often subjected to high pressures during processing (especially in injection molding) and in use. Pressure studies on polymers typically investigate the equation of state of melts, glassy, semi-crystalline, and liquid-crystalline

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* Corresponding author.

phases, and the pressure dependence of transition temperatures (melting, crystallization, glass formation, mesophase transitions, phase separation), as well as the kinetics of these transition phenomena. Some of these pressure phenomena can, of course, also be studied by extending more traditional thermoanalytical techniques (TMA, DTA, DSC) into the high-pressure region. However, *PVT* techniques offer a distinct advantage: they are inherently very quantitative. There are no "baseline" problems, because the volume is measured directly and sensitively. This makes it possible to detect even very "small" events, such as very slow crystallization or annealing in the solid state, perhaps continuing over periods of hours.

We will proceed with a short discussion of the experimental techniques involved, followed by a demonstration of the various phenomena observed (and their interpretation) in semi-crystalline polymers. Of course, the best experimental equipment is not limited in its applicability to semi-crystalline polymers (and their melts) but is just as well suited for studies of glassy polymers, liquid crystalline phases, or, for that matter, other organic solids, elastomers, solvents, solutions, other liquids, suspensions, etc.

EXPERIMENTAL *PVT* TECHNIQUES

In the literature, there are many ingenious dilatometers, i.e. devices to measure the dimensional changes of a material as a function of temperature and other variables [1]. When volume changes need to be measured because the material has liquid-like character over at least a portion of the measurement range, and when pressure needs to be included as one of the variables, two methods are widely practiced: the "piston-die technique" and the "confining fluid" technique [1].

In the piston-die technique, the material is confined in a rigid die or cylinder, which it must fill completely. A "pressure" is applied to the sample by a piston, and the movement of the piston with volume and temperature changes is used to calculate the volume change of a sample. There is a crippling fundamental problem inherent in this measurement concept, as well as many practical problems. The fundamental problem is that the state of stress for a solid sample in this type of apparatus is not hydrostatic, i.e. the sample is not under a true pressure. We have analyzed mathematically the stresses and volume changes experienced by a sample loaded axially in a rigid die (or cylinder) [2], and the situation can be very different from that of a sample under hydrostatic pressure. The main conclusion of our analysis is that this type of dilatometer can only measure volumes under "pressure" when the shear modulus of the sample is very much smaller than its bulk modulus [2]. This is certainly the case for liquids, including polymer melts. The use of such a dilatometer for studies in which the material has solid-like properties over at least part of the measurement range, however, must be avoided, because it leads to nonsensical results.

This conclusion is independent of another complication, which clearly affects results as well: often a sample that solidifies in a piston-die dilatometer sticks to the wall, and forms voids within it when it solidifies from the outside, again leading to unacceptable results. In the melt, where there are no fundamental objections to the method, another practical complication is leakage around the piston. This is often a problem when a low-viscosity polymer, or a true liquid, is tested. Designing elaborate seals invariably introduces a large amount of friction into the seal, leading to uncertainties in the "pressure" applied, and the distinct possibility of freezing the piston in place when a sample solidifies in the course of an experiment. Fundamental and practical shortcomings of the method notwithstanding, numerous machines of this type have been described (see some examples in ref. 1), with several being sold commercially [3]. Problems resulting from the factors described above are apparent in data obtained by machines of this type. It is thus not surprising that virtually all *PVT* data published in the refereed technical literature over the last ten years have been generated on *PVT* machines of the confining-fluid type.

In the confining-fluid technique, a material is surrounded at all times by a confining fluid, often mercury, and the combined volume changes of sample and confining fluid are measured by a suitable method as a function of temperature and pressure. The volume of the sample is determined by subtracting the volume change of the confining fluid. The advantage of this technique is that the sample is under hydrostatic pressure at all times, and that there are neither friction nor leakage problems. Several machines of this type have been described in the literature (see examples in ref. 1). A problem with this technique lies in potential interactions between confining fluid and sample. For mercury and polymer samples, none have every been suspected or actually observed. The precise knowledge of the *PVT* properties of the confining fluid is, of course, also required. For example, there are no published *PVT* data for mercury above about 190°C [5]. In our equipment, extrapolations are used based on high-pressure data at lower temperatures, and atmospheric pressure data over the whole temperature range. When sufficient care is taken in all these factors, accuracies such as those quoted below for the specific equipment used in our laboratory can be achieved.

The apparatus used by us to generate the data reported in this paper is a *PVT* apparatus of the confining-fluid type made by Gnomix, Inc. [4]. It is a refined and automated version of an apparatus described in the literature [5]. The sample (about 1–2 g) and the confining fluid (mercury in almost all cases, although the apparatus and software can accommodate other liquids) are contained in a rigid sample cell, one end of which is closed by a flexible bellows. This cell assembly is placed in an electrically heated pressure vessel. The motion of the bellows end is measured by a linear variable differential transformer as the temperature and/or the pressure changes. The volume change of the sample is determined from the bellows deflection, the cross-sectional area of the bellows and the *PVT* properties of the confining fluid, while also making use of a correction function obtained by recording the bellows deflection when the cell is filled with confining fluid only (done once for each cell).

The operation of the machine and the acquisition of data are controlled fully automatically by a personal computer and sophisticated software. The apparatus uses a high-pressure pump, capable of controlling the pressure to 0.1 MPa over periods of weeks, if desired. The apparatus can operate in the isothermal, isobaric and isochoric modes, as well as a mode in which the volume, temperature, and pressure are simply recorded as a function of time in selectable time intervals, while the operator retains control over pressure, temperature, or temperature rates.

The pressure range is to 200 MPa, and the temperature range extends from room temperature to above 400°C. Maximum temperature ramps are limited to 4–5°C min^{-1}, not only because of the large mass of the pressure vessel, but also by the desire to limit temperature gradients within the 1–2 g sample. In heating, the maximum scanning rate can be achieved at all temperatures. In cooling the maximum scanning rates are limited by the natural cooling rate of the apparatus from between 4–5°C min^{-1} down and 150°C, 3°C min^{-1} down to 100°C, and even lower values at lower temperatures. Using mercury as a confining fluid, the sensitivity of the apparatus is 0.0002 cm^3 g^{-1}. The absolute accuracy is 0.002 cm^3 g^{-1} to 200°C, and better than 0.004 cm^3 g^{-1} at higher temperatures (due to uncertainty in the *PVT* properties of mercury at higher temperatures, see above). A special feature is the use of a very thin nickel foil sample cup surrounding the sample [6]. This cup is deformable and open at one end. When the cell is filled with sample, sample cup, and confining fluid, it is evacuated to a vacuum of better than 4×10^{-2} Torr. Thus, all space in the measurement cell not taken up by the sample and sample cup (both inside and outside the sample cup) is taken up with confining fluid. The use of this sample cup is designed to guarantee that the sample is always under hydrostatic pressure, whether it is in the solid state when first loaded into the cell (pellets, pieces of moldings), or in the molten state, or after it resolidifies in the course of an experiment. This makes it possible to study *PVT* properties of the solid state and transitions from the solid state to the melt, and back again to the solid state, a protocol typical of thermal analysis procedures. This protocol is patently impossible to execute with a piston-type dilatometer, for which a sample needs to be melted prior to the beginning of any measurement (in order to fill the cylinder completely), thus erasing all structural information contained in the original sample. Equally, liquids of arbitrarily low viscosity, such as water [7], can also be measured without problems.

In the following, we will discuss and interpret typical data obtained on semi-crystalline polymers in the different run modes.

ISOTHERMAL *PVT* EXPERIMENTS

In this experimental mode, data are recorded along isotherms in selectable pressure intervals, usually 10 MPa, but larger pressure intervals, or smaller ones (as small as 1 MPa) may be selected. Data may also be taken from low pressures to high pressures, or vice versa. After measurements have been completed along one isotherm, the temperature is changed automatically to a new value (higher or lower temperature), and the measurements are repeated.

The lowest measured pressure point is at 10 MPa. Data below 10 MPa are generated by extrapolation using the Tait equation (see below). This procedure yields better values for the polymer volume at low pressures than a direct measurement, because many polymers contain dissolved gases, or produce gaseous degradation products at high temperatures. These gases, trapped in the cell, would lead to unusually large volumes at low pressures. Another point to be considered is adiabatic heating during compression. When a material is pressurized adiabatically (isentropically), its temperature increases according to

$$(\mathrm{d}T/\mathrm{d}P)_s = Tv/\alpha c_p \tag{1}$$

in which v is the specific volume, α the thermal expansivity, and c_p the specific heat capacity at constant pressure. Integration of this equation for typical solid and molten polymers yields temperature changes of 5–20°C for a pressure change of 100 MPa. Of course, the situation in the *PVT* machine is not adiabatic: using the automatic pump, it typically takes 6–8 min to change the pressure by 200 MPa, and some heat exchange with the pressure vessel clearly takes place. For measurements of ordinary accuracy (within the specifications stated above), this adiabatic temperature change can be ignored. However, the apparatus has the capability of inserting a hold time of arbitrary length prior to taking the data at a pressure point, in order to maintain more strictly isothermal conditions. A more detailed discussion of the role of adiabatic heating is given in our paper describing the *PVT* properties of water [7].

Figure 1 shows isothermal *PVT* measurements [8] for a highly isotactic (>96%) polypropylene (Mn ≈ 47,000, Mw ≈ 300,000). The starting sample was prepared by compression molding a disk (5 mm thick and 2.5 cm in diameter) at 210°C and a pressure of about 400 bar, followed by cooling at about 7°C min^{-1}, while the molding pressure was maintained. The starting sample had a density of 0.904 g cm^{-3}, determined by hydrostatic weighing.

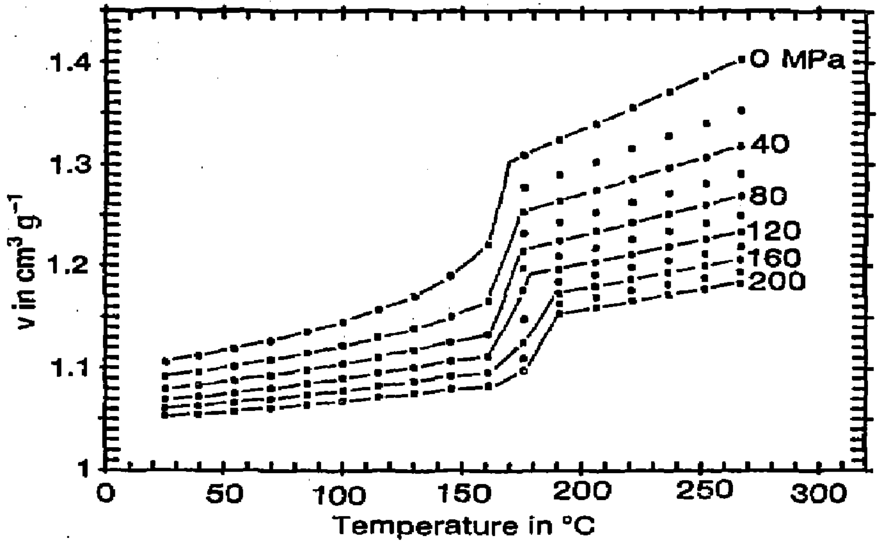

Fig. 1. *PVT* relationship of polypropylene based on isothermal measurements, progressing from low to high temperatures (but shown as cross-plotted isobars).

This disk was then cut into pieces, and pieces with a total mass of about 1.5 g were loaded into the apparatus. Data were taken in 10 MPa pressure intervals along isotherms spaced about 15°C apart, starting from room temperature, and ending at about 260°C. Rather than showing the isotherms directly, it has become customary in *PVT* work to show such data as cross-plotted isobars. The symbols shown on these cross-plots are the actual data points $v(T, P)$ at the pressures and temperatures indicated, not data based on any kind of fitting procedure. In Fig. 1, these cross-plotted isobars are shown in pressure intervals of 40 MPa at the lower temperatures, and in intervals of 20 MPa at the higher temperatures, in order not to crowd the picture. At the high-temperature end, we have the *PVT* properties of the polypropylene melt. Its isobars are effectively straight lines, although there is no fundamental reason why they should be. At low temperatures, we have the *PVT* relationship of the solid PP sample that was loaded into the measurement cell. As the temperature increases, the material clearly undergoes a melt transition, as indicated by the large volume change between 150 and 170°C. This transition region is complicated to interpret, because of the complex mode of taking the data. For example, one can observe that the zero-pressure melting transition seems to end at about 170°C. There seems to be very little change in the end of the melting interval for pressures to 140 MPa. The last statement is, however, a misinterpretation of the data for the following reason: when the melt state has been reached at the lowest pressures (10 MPa), and the melt is subsequently pressurized, as is done in this type of experiment, the question of whether or not a return to the semi-crystalline state is achieved

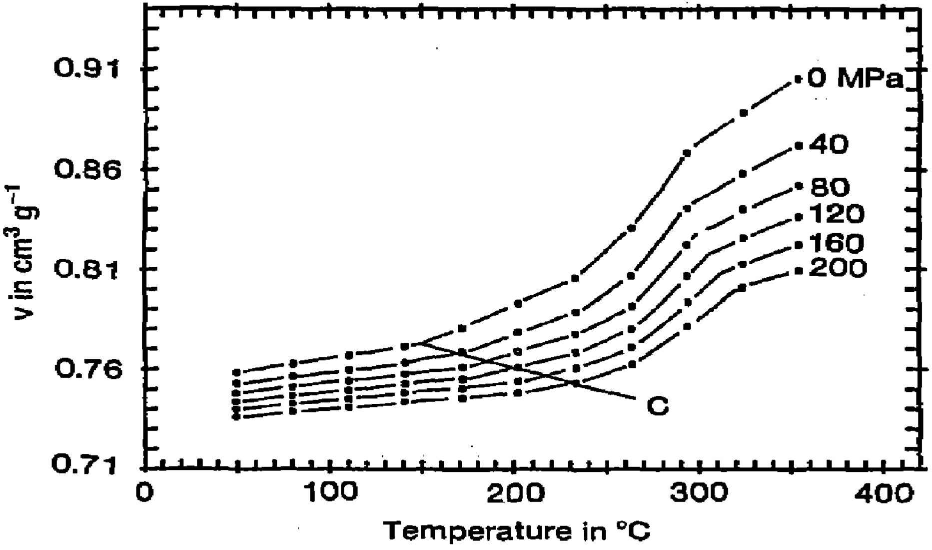

Fig. 2. *PVT* relationship of a poly(aryl ether ketone) based on isothermal measurements, progressing from high to low temperatures (but shown as cross-plotted isobars). Line C denotes the pressure-dependent glass transition.

is not just a question of the pressure dependence of the melting point, but also a question of crystallization kinetics. For this polypropylene, the melting point changes by about 30°C per 100 MPa (see below), but crystallization never takes place in the time (6–8 min) required to reach the highest pressures, except for the isotherm at 175°C, which starts out in the melt, and ends up with volumes more characteristic of the solid state at the highest pressures. In other words, the exact appearance of the "transition region" has no particular significance. The data in that region depend very strongly on the exact measurement protocol. It is best to ignore this region, and work with data in the melt region and in the solid region. Other measurement modes, especially the isobaric mode, are much better suited to study the transition region in a fundamental way.

Figure 2 shows cross-plotted isothermal data on a poly(aryl ether ketone). Isotherms were measured starting from the high end, i.e. in the melt. A solidification transition occurring in this plot between 290 and 230°C is clearly visible, as is a glass transition at lower temperatures, indicated by line C. What was said above regarding the interpretation of the main transition region applies here as well, perhaps even more so. The exact appearance of the transition region again depends on the exact protocol: the choice of the isothermal temperatures is important, as is the time between isotherms, and the rate at which the pressure is changed. Again it is best not to attempt to interpret the transition region in this type of experiment, and to study it by isobaric experiments instead, especially because there is yet another complication here: the solid state that finally develops in these kinds of experiment is not well-defined in terms of its formation history: at what pressure, and at what temperature was it initially formed? Furthermore, it is likely that structural reorganizations take place in the early times after initial solidification. Therefore, all points in the "solid state" of such a PVT diagram might not be points belonging to a material with a single internal structure, but rather to a material with a structure that changes as the experiment progresses. Below we will show evidence for such structural changes in the solid state, revealed by isobaric experiments.

Isothermal experiments are thus best used to gain a quick survey of the *PVT* relationships of a material, and to study the melt state, or the solid state of the starting sample. Melt data can easily be fitted to a variety of empirical and theoretical expressions. Among the literally dozens of expressions that have been proposed as equations of state, a relatively small number is widely used for polymers. As a successful empirical equation of state for the melt (and also the glassy state), the Tait equation recommends itself. It is generally written in the form

$$v(P,T) = v(0,T)\{1 - C\ln[1 + P/B(T)]\} \tag{2}$$

in which C is a constant, often chosen to have the "universal" value $C = 0.0894$, and B is the temperature-dependent Tait parameter:

$$B(T) = B_0\exp(-B_1T) \tag{3}$$

Together with any suitable expression for the atmospheric pressure volume, eqns. (2) and (3) represent a complete equation of state, useful for purposes of data interpolation, and calculation of derived properties.

For the record, the following equations reproduce the melt data in Fig. 1 to 0.0015 cm^3 g^{-1}

$$v(0,T) = 1.1247 + 1.041 \times 10^{-3}T$$

$$B(T) = 167\exp(-5.182 \times 10^{-3}T)$$

with T in °C, B in MPa, and v in cm^3 g^{-1}.

This level of agreement is typical for quality *PVT* data for polymer melts. Tait parameters are available in tables for a fairly large number of melts and glassy polymers [9]. It makes sense to record such values in handbooks, or encyclopedias, because melt *PVT* properties of polymers are fairly generic, i.e. they are remarkably independent of sample details, such as molecular mass (above the entanglement limit) [10, 11].

Among the theoretical equations of state proposed for polymer melts, those of Simha and Somcynsky [12], Flory et al. [13], Sanchez and Lacombe [14] and Dee and Walsh [15] are the most commonly applied. Their agreement with experimental data is generally not as good as that of the

Tait equation, which must therefore be preferred for the purpose of data manipulation, such as that required by engineers. However, the theoretical equations provided additional insight into the thermodynamics of dense polymeric systems through the interpretation of the parameters appearing within the theories in terms of chemical structure, molecular mass, etc., or their ability to predict other phenomena, such as miscibilities of polymers.

In the semi-crystalline state, the situation is more complex than in the melt. The Tait equation is generally not suitable for a good empirical description of the *PVT* relationships of a semi-crystalline polymer, and there are no theories to describe the semi-crystalline state, although theories of the equation of state of the pure polymer crystal have been developed [16, 17]. Even if a good theory of the crystal is available, it is difficult to develop descriptions of the semi-crystalline solid state for two reasons: the response of a semi-crystalline phase is sensitive to the morphology of the sample, and this morphology might continuously change as the experiment progresses. More-or-less ordered regions (amorphous and crystalline regins, in the simplest description) have markedly different thermal expansion and compressibility properties, and this leads to complex stress and strain distributions even under an applied hydrostatic stress, i.e. a true pressure. The problem is complex, and little work has been reported. We would like to recall some of our earlier work, where we compared the smaller pressure dependence of the glass transition in a semi-crystalline poly(ethylene terephthalate) (PET) with its dependence in a fully amorphous PET [18, 19]. In that case, a simple two-phase model of the semi-crystalline state combined with the requirement of equal relative volume changes in each phase (leading to an effective pressure within the amorphous part of the semi-crystalline material smaller than the applied one) was sufficient to explain the observed pressure dependences.

ISOBARIC *PVT* MEASUREMENTS

In this mode of operation, the volume is measured while a constant pressure is maintained, and the temperature is scanned, usually at a constant rate. This is the mode used by most other thermal analysis techniques, except of course that a pressure is applied to the sample. Therefore, all phenomena normally observed with thermal analysis techniques can be measured as a function of pressure. Among them are melting temperatures, the crystallization temperatures, glass transitions, mesophase transitions, phase separation, annealing processes, etc. The volume is still measured quantitatively; in fact in an equilibrium phase it is expected that the volume is independent of the measurement mode (isothermal or isobaric).

As indicated above, the pressure dependence of the glass transition in semi-crystalline materials may be strongly affected by the degree of crystallinity, and details of the morphology. Other factors, such as the scan rate, play a role similar to that observed with other thermoanalytical techniques. The same factors affect the melting point, here defined as the end of the melting interval in heating (see below). Of course, in a pressure device, it is easily possible to produce a wide variety of sample structures "in situ", because of the possibility of forming a solid sample under pressure. Pressure formation can lead to higher levels of crystallinity and unusual (often extended chain) morphologies [8, 20–25], or even different crystal structures [8, 21–23, 26–28]. It is therefore always important to have a well-characterized starting sample with which to initiate an isobaric temperature scan.

Examples of isobaric scans are given in Fig. 3. Polypropylene samples molded in a certain way were heated at 2.5°C $\min^{-1}$ at pressures of 10, 100 and 200 MPa, followed by cooling at the same pressure and rate [8]. For each heating run, a fresh, identically prepared sample was used. On heating, the end of the melting interval is clearly visible, and easily defined, as indicated on the 10 MPa curve. We chose to call the end of the melting interval the "melting point". This can be defended on the basis that the end of the melting interval is the point at which the most perfect and largest crystals melt. This temperature therefore approaches an "equilibrium" melting point more closely than other definitions. We are aware of the fact that the most commonly used procedure in DTA and DSC work is to use the peak in the thermogram as T_m, which would correspond to the steepest point on the v versus T line in PVT work. This point can, of course, also be

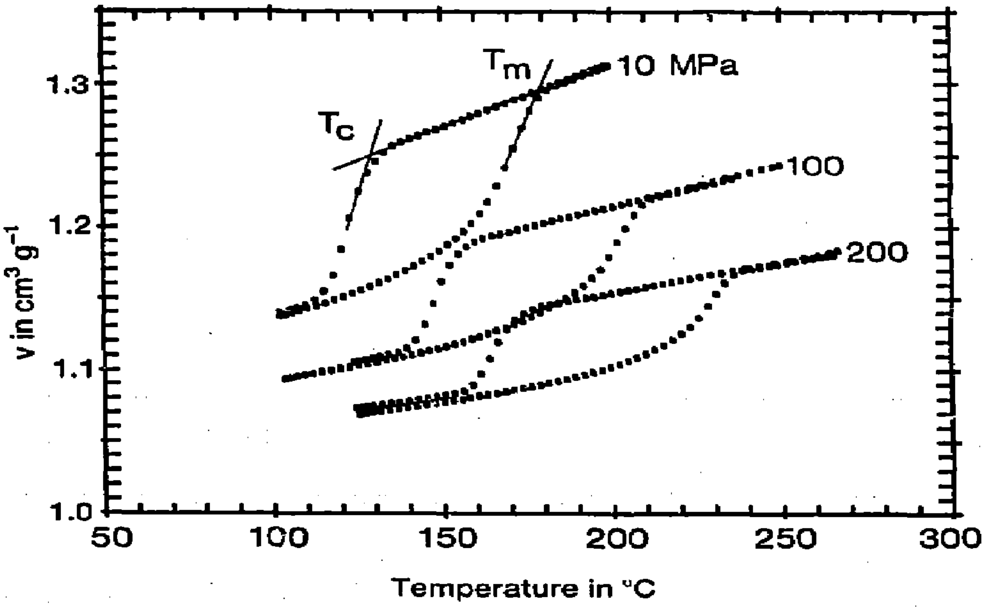

Fig. 3. Heating and cooling isobars of polypropylene at different pressures (2.5°C $\min^{-1}$), showing the definitions of the melting point T_m and the onset of crystallization T_c.

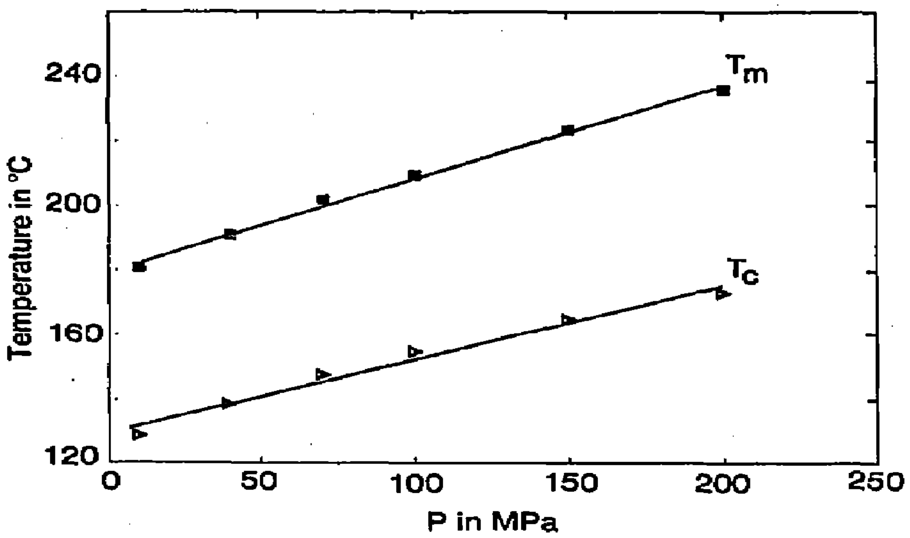

Fig. 4. Pressure dependence of T_m and T_c (defined in Fig. 3) for cooling and heating rates of 2.5°C min^{-1}.

determined from *PVT* work, and would be more comparable with melting points determined from DSC or DTA by the "peak" procedure. After extending the scan a short distance into the melt, the temperature direction is reversed. Volumes on heating and cooling superimpose almost exactly, as one would expect in the absence of degradation. The samples supercool well below the melting point, with the onset of crystallization T_c defined as indicated in Fig. 3. It is interesting to note that on cooling the volume never quite reaches that which the material had when it was first heated; this is most noticeable at the highest pressure. The reason is that polypropylene crystallizes in part into the triclinic γ-form when it crystallizes under pressure [8, 21–23]. The γ-form has a somewhat larger specific volume than the "normal", monoclinic α-form.

From a series of such scans, the pressure dependence of T_m and T_c can be established. Values for this particular polypropylene are plotted in Fig. 4, and fitting yielded the following pressure dependences

$$T_m = 179.2 + 0.290P \tag{4}$$

$$T_c = 129.3 + 0.229P \tag{5}$$

with temperatures in °C, and pressure in MPa.

These pressure dependences are in line with values of dT_m/dP of between about 0.10 and 0.95°C MPa^{-1} found for a wide variety of semi-crystalline polymers [29]. Another feature expressed by eqns. (4) and (5) is that the supercooling, $T_m(P) - T_c(P)$, is reasonably independent of pressure, changing from about 50°C at $P = 0$ to 62°C at $P = 200$ MPa. This slow pressure dependence of supercooling is observed for a wide variety of crystallizable polymers, although there are exceptions, sometimes associated with a change in crystal structure, or the formation of extended-chain crystals.

The crystallization temperature, and with it the amount of supercooling observed, of course, depend on the cooling rate, and on the presence of crystallization promoters. Crystallization temperatures and supercooling are therefore values characteristic only of a specific polymer formulation within a generic class, and not characteristic of a whole glass of polymers.

The pressure dependence of the melting point can be used in a very interesting and useful way. It permits the calculation of the heat of fusion Δh_f of a polymer crystal through the application of the Clapeyron equation. Because polymers cannot, in general, be obtained in a completely crystalline form, it is not possible to measure the heat of fusion of the crystal directly. In general, a series of experiments involving density determinations, heats of fusion, and perhaps infrared studies of samples with different crystallinities (differ formation histories) is used to arrive at a value of the heat of fusion of the crystal. Such schemes, though appearing to be self-consistent, can lead to a totally incorrect value of the heat of fusion [30]. The scheme involving the Clapeyron equation is more direct. The Clapeyron equation is

$$\Delta h_f = (T_m \Delta v)/(\mathrm{d}T_m/\mathrm{d}P) \qquad (6)$$

where T_m is the melting point, and $\Delta v = v_a - v_c$, where v_a and v_c are the specific volumes of the melt and the crystal, respectively, at the melting point.

Normally this equation is evaluated at the atmospheric pressure melting point, and $\mathrm{d}T_m/\mathrm{d}P$ is the pressure dependence of the melting point at atmospheric pressure. To obtain $\mathrm{d}T_m/\mathrm{d}P$, one must, of course, use a consistent definition of the melting point at each pressure (for example the one proposed above), and one must use the melting point of a sample with the same structure for each pressure run. That is why we use a fresh, identically prepared sample for each heating run, i.e. for each pressure. All quantities needed for a calculation of the heat of fusion are obtainable from *PVT* measurements, except for the crystal volume at the melting point. For this, X-ray diffraction at temperatures close to the melting point can be used. This method based on the Clapeyron equation is a conceptually very straightforward (albeit experimentally demanding) way of obtaining the heat of fusion of a crystal. Its accuracy is mainly limited by the determination of the crystal volume v_c. Under the best of circumstances, unit cell volume determinations close to the melting point are accurate to perhaps 1–2%. In some material there is a progressive loss of X-ray diffraction lines as the melting point is approached, and the uncertainty in v_c is much larger [30–33]. Because the volume change Δv on melting is often only 10% of the actual volumes, this introduces a sizeable

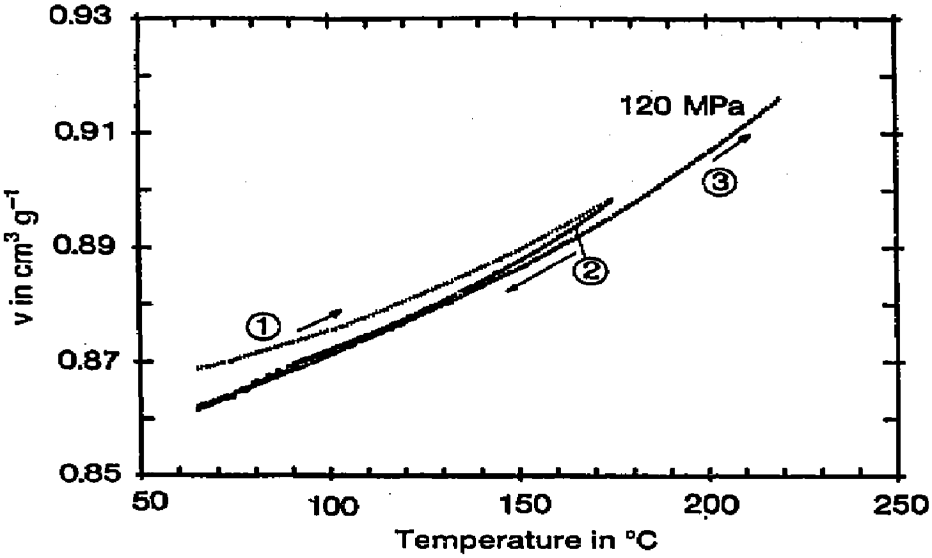

Fig. 5. Annealing processes in the solid state of polyamide 6 (see text).

error into the determination of Δh_f, typically 10% or more. Even then this method has lead to significant revisions of some values of the heat of fusion [30, 31], while in other cases it has confirmed existing values [32, 33]. In cases where a major revision resulted, we believe that the new values, determined via the Clapeyron equation, are in better agreement with other known facts about the polymers concerned.

The *PVT* method is also sensitive enough to follow solid-state reorganizations through the change in volume associated with them. Because there are no baseline problems as in DTA/DSC, very slow processes, lasting hours or even days, can be followed. As an example, we present data on a polyamide 6 in Fig. 5. Individual data points are recorded and plotted at 1°C intervals. All traces were obtained at 120 MPa. In trace 1, a solid PA 6 sample was heated to about 170°C at a rate of 2.5°C min^{-1}. The starting sample had been compression molded at 270°C and a pressure of about 200 bar (20 MPa), followed by cooling to room temperature at a rate of about 8°C min^{-1}, before loading into the cell of the *PVT* apparatus. Following the recording of trace 1 in Fig. 5, the sample was cooled at a rate of 2.5°C min^{-1}, still at a pressure of 120 MPa (trace 2). The "jitter" in trace 2 below about 90°C was caused by an experimental problem with the apparatus (corrected since then), but does not detract from the overall phenomenon. It can be seen that, except in the vicinity of the turnaround point, the cooling trace does not follow the first heating trace, but stays below it (higher density). This means that during the measuring of trace 1, and perhaps during the measurement of trace 2, slow structural changes towards higher density occurred. On reaching 60°C, the sample was heated up once again (trace 3). At the reversal point the volumes are independent of the direction of temperature change, in fact trace 3 follows trace 2 (within better than 0.001 $cm^3 g^{-1}$) up to 130°C or so, and then stays below it, indicating that more structural changes have occurred during the recording of trace 2 or trace 3. We are not able in this paper to discuss the physics of these changes, nor the role that pressure plays in these annealing processes. Our purpose is to demonstrate that confining-fluid *PVT* techniques can follow these slow changes as they are occurring, and with great sensitivity. In addition, we believe that these phenomena are not related to degradation, but are physical phenomena occurring entirely within the solid state. Heating into the melt following trace 3 and subsequent cooling from the melt shows normal crystallization behavior. On this basis we exclude degradation effects, which are known to affect the crystallization behavior significantly [3].

CRYSTALLIZATION KINETICS MEASUREMENTS AT ELEVATED PRESSURES

Yet another mode of operation of *PVT* equipment was used in a fundamental study of crystallization kinetics at elevated pressures. In this mode, both the temperature and the pressure are kept constant. If a sample is in the melt or in an unchanging solid state, its volume will, of course, stay constant with time. If, however, crystallization occurs, the volume will decrease as a function of time.

With respect to Fig. 4, it is possible to delineate the region in the $P-T$ plane where such experiments have a chance of succeeding. Obviously, above the $T_m(P)$ line, a material will stay in the melt indefinitely, whereas in the vicinity of the $T_c(P)$ line, crystallization may be sufficiently fast to prevent approaching certain (P, T) conditions without crystallization occurring on the way to the (P, T) point. Therefore, achievable experimental conditions fall below the $T_m(P)$ line and somewhat above the $T_c(P)$ line of a material.

Jing He [8] explored the pressure crystallizations of polypropylene, polyamide 66 and poly(ethylene terephthalate) during her thesis work at the University of Colorado. Again, the purpose of this paper is not to discuss the polymer physics of what we observed, but rather to demonstrate the capabilities of the *PVT* technique. We will use some examples from her work on polypropylene. She explored crystallization at about 40 points in the $P-T$ plane, involving temperatures between 130 and 190°C, and pressures between 10 and 200 MPa. Under these conditions, crystallization took anywhere from 10 min to 24 h to complete. At the beginning of each experiment, a sample was heated to 200°C at 10 MPa, to insure complete melting. It was next cooled at 10 MPa to the experimental temperature within 10–25 min. Next, the pressure was increased to the experimental values over a period of a few minutes. An example of this cooling process,

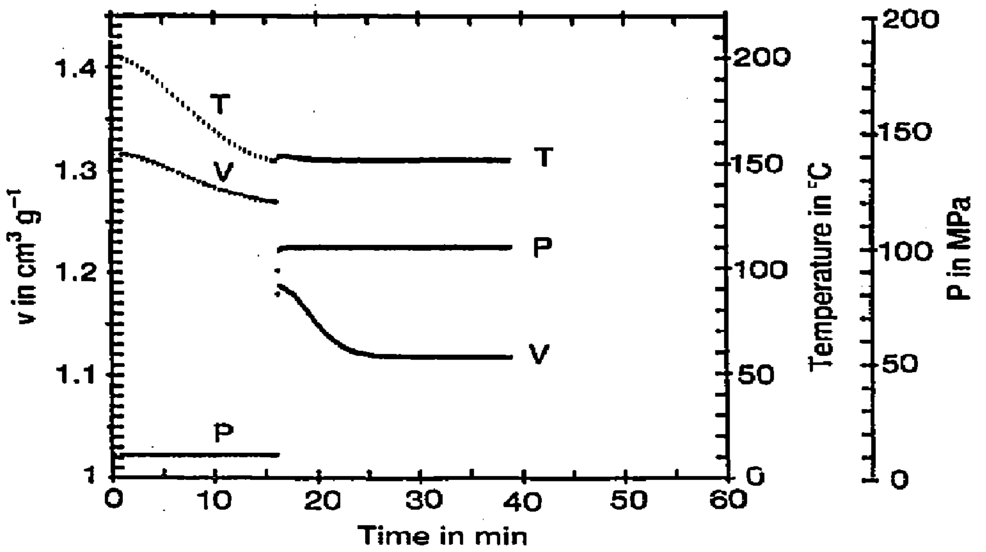

Fig. 6. Crystallization of polypropylene at a constant pressure of 100 MPa and a constant temperature of 152°C.

and the subsequent crystallization at 100 MPa and 152°C is shown in Fig. 6. Volume changes during crystallization were next plotted in the form suggested by the well-known Avrami equation (Fig. 7) [8], and fitting was used to determine the Avrami rate constant Z, and the Avrami exponent n. We found $n = 1.3–1.7$, without a clear dependence of n on the temperature and pressure of crystallization, except that the n values at higher pressures

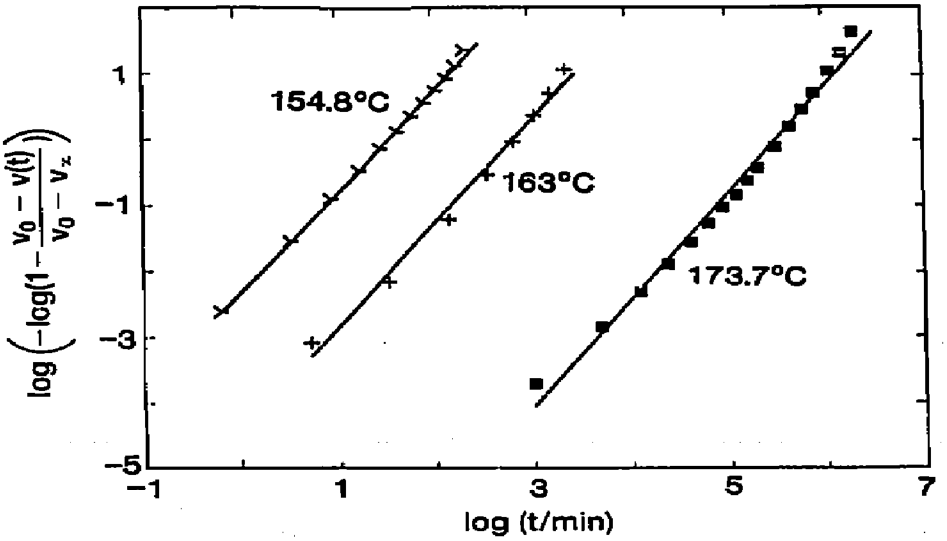

Fig. 7. Avrami plots of crystallization of polypropylene at 100 MPa and different temperatures: v_0 is the specific volume at the beginning of crystallization ($t = 0$); $v(t)$ the specific volume at time t during crystallization; and v_∞ the specific volume at the end of crystallization.

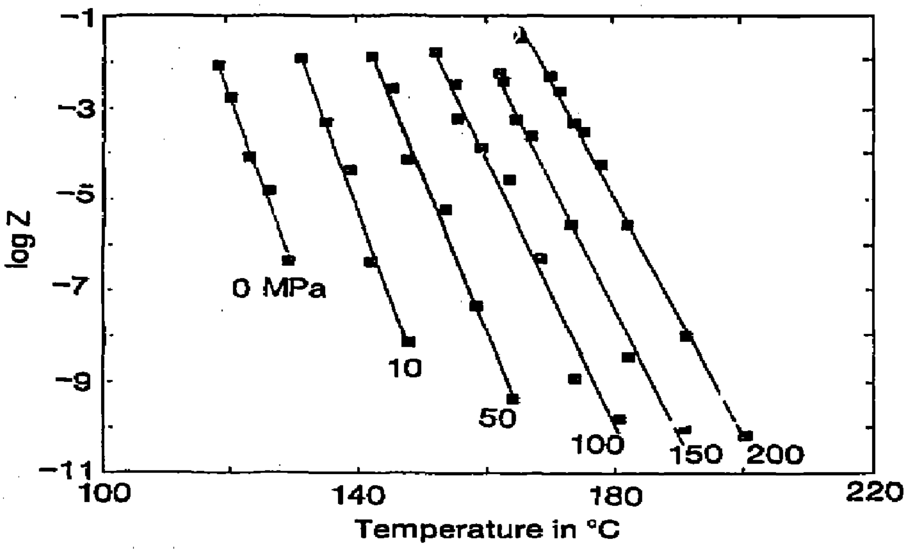

Fig. 8. Avrami rate constant for polypropylene versus temperature at different pressures.

were perhaps slightly higher than those at low pressures. This may be a consequence of the appearance of the γ-form crystals at higher pressures [8, 21–23], but has no significant effect on the crystallization kinetics.

In Fig. 8 the rate constants obtained at various pressures are plotted against temperature. The regular behavior over the whole pressure and temperature range is apparent. These rate constants can be plotted in another, very revealing way. In Fig. 9 we have once again plotted the $T_m(P)$ and $T_c(P)$ lines from Fig. 4. Superimposed on this, we show loci of constant

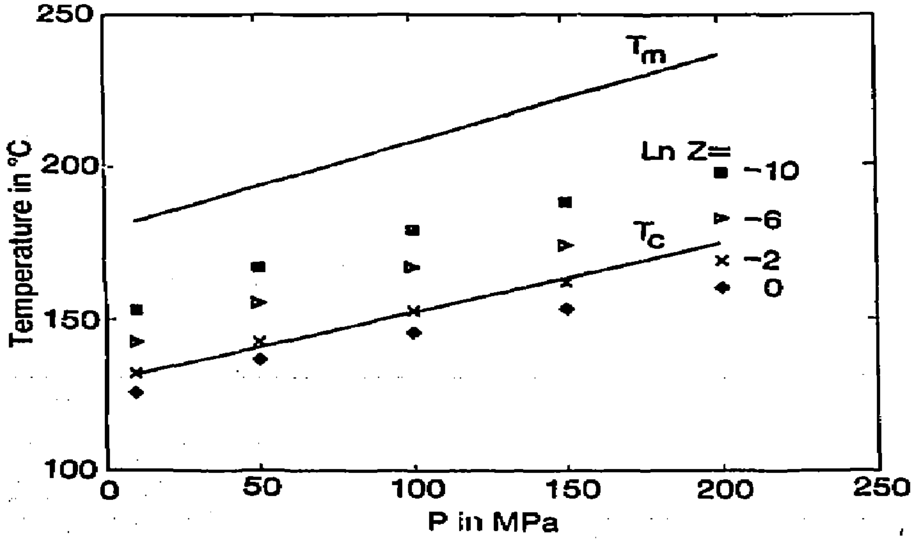

Fig. 9. Loci of constant Avrami rate constant Z (for values of ln Z given in the figure) of polypropylene in the P–T plane, superimposed on the pressure dependence of T_m and T_c.

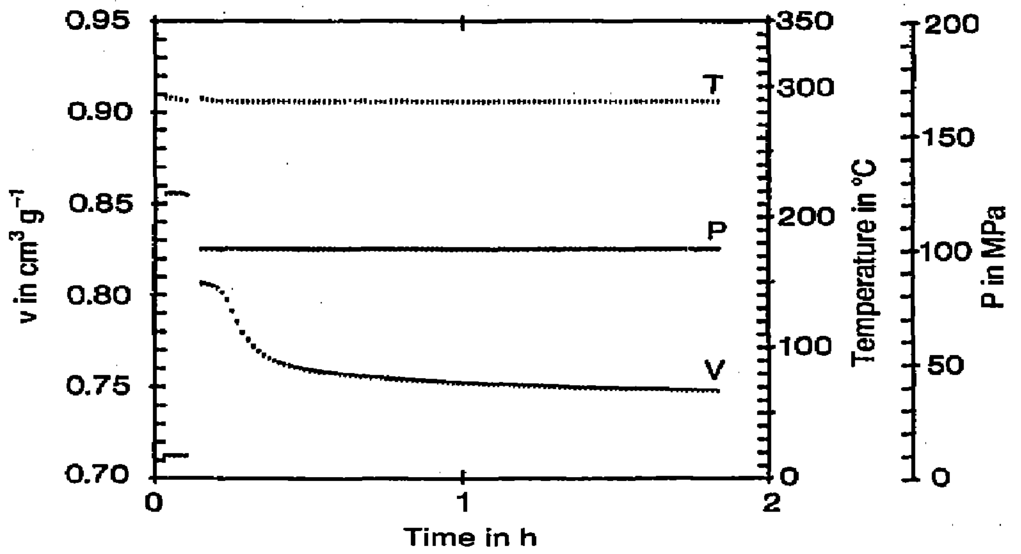

Fig. 10. Crystallization of poly(ethylene terephthalate) at 100 MPa and 289°C, demonstrating the slow secondary crystallization.

Avrami rate constant Z. It is very intriguing to see that lines of constant Z are substantially parallel to the T_c line. This is an extremely simple result: it permits the prediction of crystallization rates at higher pressures from crystallization information at low pressures and a knowledge of the $T_c(P)$ dependence. If this were generally true for polymers, it could substantially reduce the amount of *PVT* work needed to obtain a picture of pressure crystallization for a particular material. We suspect this finding will hold for many polymers, at least we have not seen anything to the contrary in polyamide 66 [88] or poly(ethylene terephthalate [8], although the latter material's crystallization kinetics are not well described by the Avrami equation, due to a very long-lasting secondary crystallization phase, evident in Fig. 10.

APPLICATIONS TO MOLDING TECHNOLOGY

The simulation of processes occurring during the melt processing of polymers has become a major activity within polymer engineering in the last few years. Many of these activities are aimed at the prediction of flow, stresses, and shrinkage in the injection molding process, which often involves pressures to 150 or 200 MPa. The *PVT* properties of a material can be expected to be an important input into such modeling software, already commercially produced by several companies [34], because volume changes between the melt state and the solid state are often 10–35% and are strongly affected by pressure. While *PVT* properties thus clearly enter into the picture, the method by which this should be done is not at all clear. Different university and industrial researchers and commercial software companies use their own insight, and sometimes do not reveal how they are using *PVT* data. One of the major problems is, of course, that molding often involves cooling rates of several hundred °C min^{-1}; this particular apparatus is limited to 5°C min^{-1}. In our opinion, there is no hope of simulating the actual high cooling rates observed during molding in a *PVT* apparatus—after all, even DSC equipment with sample sizes of just a few milligrams is limited to rates of perhaps 50°C min^{-1}. Nevertheless, *PVT* data are currently used by all people developing or selling processing software, and in the future we expect that the application of *PVT* data will continue to grow in sophistication. One route is, perhaps, the use of actual crystallization kinetics data, such as those described above, and extrapolated to shorter times.

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