

# **THE THERMAL ANALYSIS OF POLYMERS AT HIGH PRESSURES**

*P. Zoller and P. French*

University of Colorado, Department of Mechanical Engineering, Campus Box 427, Boulder, CO 80309-0427, USA

## **Abstract**

The extension of two techniques of thermal analysis into the region high pressures (50–100 MPa) are discussed. One is the extension of dilatometry (thus becoming pressure-volume-temperature measurements, PVT). This technique has been well established over the past few years. Some results obtained on typical polymer systems are presented and discussed. The second is the extension of the differential thermal analysis (DTA) principle to high pressures, trying to maintain some of the advantages of the DTA technique when compared to the PVT method, such as small sample size and productivity. DTA determinations of the pressure dependence of the melting points of pure metals and polymers are presented and compared with results from the PVT technique. Satisfactory agreement is obtained. The advantages and limitations of our current high-pressure DTA method are discussed.

**Keywords:** dilatometry, high-pressure DTA, pressure-volume-temperature measurements

## **Introduction**

The extension of thermal analysis techniques to high pressures is of interest to materials scientists and engineers. This is self-evident, not only because materials often encounter high pressure environments during processing or use, but also because the inclusion of pressure as a variable leads to a more complete thermal description of a material, and can provide new scientific insights.

By thermal analysis techniques we mean not only the enthalpic techniques, such as differential thermal analysis (DTA), or differential scanning calorimetry (DSC) but also dilatometry and other relevant methods, including thermal transport measurements. This paper will consider the extension of dilatometry to high pressures of 200 MPa (2 kbar) (thus becoming pressure-volume-temperature, PVT, measurements), as well as DTA techniques to the same pressures. PVT studies are an area in which our lab has been active for many years. Our techniques have been developed to a high degree of perfection and have been recognized for a number of years. A particular incarnation of the equipment has been made available commercially [1]. We have put much less effort

into high-pressure DTA measurements, but have reached a point where certain kinds of results can be obtained. Since there is overlap between the results of DTA and PVT techniques, some results can be compared. It is thus the purpose of this paper to present experimental high pressure PVT and DTA techniques, to discuss their advantages and disadvantages, and to compare results from both techniques where possible.

On the most fundamental level, the inclusion of pressure as a variable can lead to a much more complete thermal description of a material. For example: it is well known that the knowledge of the equation of state of an equilibrium phase, together with a knowledge of the specific heat along any path (for example as a function of temperature at atmospheric pressure) furnishes a complete thermodynamic description of the phase, permitting, in principle, the calculation of any thermodynamic function. For this reason PVT measurements (yielding an equation of state) play a more fundamental role than the mere extension of enthalpic techniques to higher pressures. For example, the pressure dependence of the specific heat can be calculated from the equation of state as:

$$(\partial C_P / \partial P)_T = -T(\partial^2 V / \partial T^2)_P$$

Of course, PVT data employed for this purpose must be of the very highest quality, since the double numerical differentiation required by this equation is difficult, magnifying scatter or systematic errors in the data strongly. But: PVT data can be of very high quality, and they are less open to interpretation than some other thermal analysis techniques. Volume is volume – "baselines" do not enter the data interpretation in PVT measurements as they do in various enthalpic thermal analysis techniques.

Of course, pressure studies are not limited in the kinds of materials to be investigated, but they are especially important in the area of solid and molten polymers. In polymer science the inclusion of pressure is of very useful for any study relating to concepts of "free volume". A large range of polymer physical research relates to the nature and behavior of this "free volume". Diffusion, rheological studies, other dynamic phenomena, melting, crystallization, and the nature of the glass transition are invariably couched in terms of "free volume". At atmospheric pressure, changes in free volume are automatically tied to variations in temperature. By using pressure as a variable, free volume and temperature can be largely de-coupled, and its use is put on a more solid footing. The quantification of "free volume" has also been a problem, being somewhat arbitrary. However, the "hole fraction" parameter from the theoretical equation of state of Simha and Somcynsky [2] may offer itself as such a parameter. It can be calculated unambiguously as a function of temperature and pressure for an equilibrium polymer phase (the melt, in most cases) by fitting the theoretical equation of state they developed to experimental PVT data.

On the other end of the interest in the behavior of polymers at high pressures are the engineering questions of thermal expansion, compressibility (bulk modulus), pressure dependence of transition temperatures, and related questions. While, of course, these questions are of interest to polymers physicists as well, they do indeed have special applications in polymer engineering, mostly in the area of processing. Much polymer processing takes place at elevated pressures, to 100 or even 200 MPa in the case of injection molding, and it is of paramount importance to understand how high pressures affect the thermal expansion of melts and solids, their compressibility, the shifts of melting and glass transition temperatures, and the crystallization kinetics itself. It is in this area that pressure data are most widely applied, often in the simulations of the molding process by computer codes, widely used in the processing industry [3].

## Experimental techniques

### *Pressure-volume-temperature measurements*

#### The confining fluid technique

Pressure-volume-temperature techniques have developed along two distinct lines: the confining fluid method, and the piston-die method.

In the confining fluid technique [1, 4, 5], a material (liquid, solid, pasty, or anything else) is surrounded by a fluid, contained in a piezometer cell, closed at one end by a flexible bellows. Mercury is most commonly used as the confining fluid in PVT studies of polymers, since virtually all polymers are inert to mercury. The closed piezometer cell is placed in a pressure vessel, and pressures to 200 MPa, typically, are applied by a pressurizing fluid, generally a heat-stabilized silicon oil.

The pressure is transmitted to the contents of the piezometer cell by the flexible bellows, which contracts or expands in response to pressure and temperature changes in the contents of the piezometer cell. The motion of the bellows is used to calculate the volume changes of the cell contents (using the effective cross-sectional area of the bellows), and the volume change of the sample is obtained by subtracting the volume change of the confining fluid, which must be known, or must be measured in the PVT apparatus itself prior to its use as a confining fluid.

A well-designed machine of this type is capable of great sensitivity (to  $0.0002 \text{ cm}^3 \text{ g}^{-1}$ ) and absolute accuracy ( $0.002$  to  $0.004 \text{ cm}^3 \text{ g}^{-1}$ , depending on temperature range). The great advantage of the techniques is that a sample is always under hydrostatic state of stress, whether it is a solid or a liquid, or anything else, and while it changes from a solid to a liquid state, or from a liquid to a solid (i.e. during crystallization, melting, glass formation, mesophase transitions in liquid crystalline system, etc.). Because of the large density differ-

ences between mercury and typical polymers, a special technique ("sample cup") [6] has been developed to keep the sample surrounded by mercury at all times, thus insuring a hydrostatic state of stress (i.e. a true pressure) throughout an experiment. Hydrostatic state of stress can not be maintained in samples which are not true liquids in the "piston-die technique" described below, making it unsuitable for measurements in and out of liquid and non-liquid (solid, liquid crystalline) states [7].

The commercial machine [1] based on this principle [5] offers complex PVT measurements with full automation, presenting on line data in several modes: isothermal, isobaric, constant volume, or combinations of these, over a temperature range from ambient to more than 400°C, and pressures to 200 MPa. Samples are typically 0.5 to 1.5 g. Because of this, and the massive size of pressure vessels required, temperature changes are limited to 3–5°C min<sup>-1</sup>. Virtually all PVT studies reported in the refereed scientific and technical literature in the last 10 years has been measured using this technique.

### The piston-die technique

This method is deceptively simple. A material is contained in a rigid, closed-end tube or cylinder (the "die") and is "pressurized" by a piston [4]. The motion of the piston is used to calculate the volume changes in the sample with temperature or "pressure" changes. This technique requires that sample completely fill the tube or die, which can only be achieved with a molten sample. Therefore, samples can not be used in the state in which they are submitted for testing, e.g. in pellet form, or in the form in which they come out of a molding operation, but must first be melted, destroying his pre-history. Studying the effect of previous history is of great importance in thermal analysis, and the inability to test "as received" samples is definitely a problem of the technique, and would not be acceptable in differential thermal analysis, for example. Moreover, in this type of a device, the state of stress for a solid sample (solidified in situ from the initially molten sample) is no longer hydrostatic, leading to imprecise or nonsensical results. This is the reason why we use quotation marks around the word "pressure" in the context of this principle. The question of leakage around the piston, or piston friction, leading to unknown "pressures", are difficult practical problems, always encountered, which lessen the accuracy of the technique. We have extensively commented on all these areas [4, 6–8]. There are several commercial machines based on this principle, but we know of no technical articles in the refereed literature based on this technique in the last 10 years.

### *High-pressure differential thermal analysis*

A fairly large number of studies have been reported, extending the well-known DTA or DSC techniques to high pressures (50–200 MPa, or more). This

paper does not claim to be a review of previous work, but, instead, Refs [9–18] illustrate commonly encountered design problems and possible solutions which we considered when we started this project in 1989. Because of the nature of the studies envisioned for their systems, different investigators required different pressure capabilities, and designed for different temperature ranges, including temperatures below ambient in some cases. We aimed at a temperature between ambient and about 400°C, and pressures to 200 MPa. This seemed appropriate for a large class of studies of polymers. A goal, naturally, was also to devise a high-pressure DTA that would offer the sensitivity, ease of use, range of heating/cooling rates, safety and productivity of the well-known commercial machines operating only at or near atmospheric pressures. This, it turns out, is probably impossible because of fundamental reasons, and many compromises need to be made.

The choice of a pressure transmitting medium especially needs to be considered carefully. A gas-pressurized system must be considered dangerous, because of the large energy stored in a pressurized gas. Because of the dangers inherent in this type of system, they are generally operated in steel or concrete bunkers. A gas system would offer advantages in the moderate degree of thermal coupling provided between sample and oven, and between sample and reference side. Nevertheless it is apparently very difficult to perform quantitative work (heat of fusion and such), because the thermal diffusivity of a gas, and with it the coupling between sample and oven, changes with pressure. In general systems were only calibrated at atmospheric pressure. As it turns out, a liquid-pressurized system, while not suffering from the safety problem, leads to a strong coupling between sample and oven, which reduces the sensitivity. This coupling is also variable with pressure and temperature, but certainly less so than that of a pressurized gas.

Another problem recognized, and often leading to complicated and cumbersome solutions, is the need to separate the pressure transmitting medium and the sample. This is an absolute requirement in our opinion, since any kind of chemical or physical interaction between sample and pressure-transmitting medium would likely be associated with thermal effects, and might lead to modifications of the sample itself. Even dissolution and solution of gases (in gas pressurized systems) leads to thermal events, and perhaps the formation of a foam of a polymer sample, further altering the thermal situation.

Some procedures described required thermal treatment of samples, such as melting, as part of the sample mounting technique. Since the purpose of thermal analysis often is to study samples produced in some processing operation, we considered further thermal treatments solely for the purpose of sample mounting something to be avoided at all cost, just as it is unacceptable to have to melt a sample prior to its use in a piston-die PVT apparatus.

With all these problems in mind, we will simply discuss some of the approaches we have taken to reduce these problems to a level where some high

DTA measurements could be performed with reasonable effort. The result is a fairly productive unit, which can measure the pressure dependence of melting, crystallization and glass transitions, but is not yet quantitative, and thus unable to measure heats of fusion, and or specific heats with any accuracy.

### *The University of Colorado high-pressure DTA system*

The apparatus we designed has not been described in the literature, except in two theses for the degree of Master of Science in Engineering at the University of Colorado [19, 20]. The apparatus is based on the temperature difference principle (DTA principle). A horizontal pressure vessel contains sample and reference thermocouples of a sheathed, commercial type. We chose to arrange the sample and reference pans along a horizontal axis in order to reduce convection in the vessel. The vessel is about 150 mm long with an outside diameter of 30 mm, and an inside diameter of 12.5 mm. Sealing is by applying an axial force (of about 50–60 kN, supplied by a hydraulic ram) to the end pieces. On each side, three sheathed type *K* thermocouples (1 mm sheath diameter) are inserted into the pressure vessel. The tips of the three thermocouples are contained in a plane perpendicular to the axis of the pressure vessel, and the tips lie 60° apart on a circle of approximately 5 mm diameter. The sample and references are contained in sample pans marketed in the past for the Mettler TA2000 thermal analysis system. These pans have a convenient small attached tip on the bottom half. We screw a 1.5 mm diameter stainless steel rod to the tip on the pan in a special fixture. This rod, in turn, is attached to a spring assembly when placed in the DTA, the spring pulling the bottom of the reference and sample pans with a well-defined force against the three thermocouples on each side. This arrangement provides pretty reproducible thermal contact between sample and reference pans and the respective thermocouples, and this contact is maintained as the temperature and the pressure change.

As previously stated, we attached high priority to separating the sample from the pressurizing oil. We have developed a technique to etch the commercial aluminum pans, such that, when assembled in the normal Mettler pan crimper, the top and bottom fused together and did not develop leaks when used in the high-pressure DTA. Success of this method usually requires us to fill the pan completely, occasionally by adding an inert substance to a sample. If the sample (and filler) do not take up most of the space in the pan, too much deformation of the pan may take place when pressure is applied, and the pan may actually tear. If no tearing occurs, the sample remains separated from the pressure medium, and the thinness of the pan assures transmittal of essentially the full pressure to the contents of the pan.

The pressure vessel (oven) is surrounded by a 10 mm thick shell of copper to make the temperature more uniform. The oven is heated electrically with two

balanced band heaters, using a simple controller with a setpoint controlled by the system's software to produce the desired scan rate. Heating rates to  $10^{\circ}\text{C min}^{-1}$  can be achieved over most of the temperature range. Currently there is no provision for forced cooling, except for some fans. Controlled cooling rates of more than  $10^{\circ}\text{C min}^{-1}$  can only be achieved at temperatures above  $200^{\circ}\text{C}$ , with the maximum cooling rate limited to  $2^{\circ}\text{C min}^{-1}$  between  $50$  and  $100^{\circ}\text{C}$ . This could obviously be improved by including forced cooling of a more sophisticated kind, but the massive nature of the pressure vessel makes the system inherently less responsive than common atmospheric pressure DTA systems.

For pressurization we use a heat stabilized silicon oil. It is pumped by a small hand pump. Pressures are measured with a digital pressure gauge with 0.3% accuracy and are output to a computer for pressure recording. Although we have a lot of experience in the area of automatic control of pressure to 200 MPa from our PVT work, we do not at present use such automatic control in the DTA system. Instead we simply set a pressure, and then close off the pressure vessel. Naturally, the pressure in this closed system will increase as the pressure vessel is heated, and decrease with cooling. After increasing the volume of the closed system by adding a dummy pressure vessel, the pressure increased by less than 5 MPa for an increase in temperature of  $100^{\circ}\text{C}$ . This turned out to be satisfactorily slow, and we simply associate thermal events with the pressure recorded at the same time. In future versions of this apparatus we might include a proper pressure control – but this might not be unproblematic, since any pressure adjustment in the measurement cell (pressure vessel) would produce a concomitant temperature shift because of adiabatic heating or cooling. In addition any oil pumped into the pressure vessel would be at a temperature different from that already in the pressure vessel, again producing a thermal event.

Two thermocouples from each side are wired together to produce the differential temperature between sample and reference side. This signal is next amplified in a highly stable DC amplifier from a Mettler TA2000 system, before being fed into the computer. The third thermocouple on each side is used to either measure the reference or the sample temperature.

Software written to run this system provides for data collection in appropriate time intervals (pressure, differential temperature, temperature of reference thermocouple), graphic display of data, storage and evaluation of data, as well as providing temperature control to the system.

## Examples of high-pressure studies

### *PVT measurements*

In the following, we wish to present and discuss typical PVT data obtained on a liquid, an amorphous polymer, a semi-crystalline polymer, and a polymer

which remains solid over the whole range of measurements. These are simply examples of typical behavior, illustrating the precision and power of the technique, while giving some references to more detailed studies. However, it must be realized that literally thousands of materials have been run through GNOMIX machines alone. A larger collection of representative data (about 200 materials) has been published [21], but even that collection will only scratch the surface. One must also realize that within generic classes of materials, there are subtle but important differences among specific formulations, and that only direct measurement of a specific material can characterize it fully. All samples were measured using a GNOMIX apparatus in the lab of the authors at the University of Colorado.

#### Example 1: PVT studies of a liquid

Many solids, of course, become liquid as the temperature increases (see the examples of amorphous and semi-crystalline polymers, below), but PVT measurements can also be made of samples which are liquid even at ambient temperatures. In the past we have presented such data, most notably a study of the equation of state of water primarily as a test of the precision of the apparatus [22]. In this paper we present the PVT relationships of a perfluoroether fluid (Krytox<sup>®</sup> fluid, DuPont). At room temperature this is a fluid of about 500 cSt viscosity. Measurements of the specific volume were performed along isotherms, located from ambient temperatures to about 310°C in 10°C intervals. Along each isotherm, volumes were recorded in pressure intervals from 10 to 200 MPa, in 10 MPa intervals. A point for zero (atmospheric) pressure was obtained by extrapolation of data from 10 to 30 MPa in 1 MPa increments. This protocol is executed fully automatically, but the time required is perhaps 8–9 h. In Fig. 1 some of the data are plotted as cross-plotted isobars, in 40 MPa increments. Since this material remains liquid at all temperatures and pressures during this study, no transitions are apparent. The dependence of the volume on temperature and pressure is very strong, however. Note that the volume expansion at zero (atmospheric) pressure between ambient temperature and 300°C is more than 50%, and that the compressibility, especially at the higher temperatures, is strongly pressure dependent. It is possible to fit well-fitting functions to data of this type, so that the equation of state is available in a convenient mathematical form to be used for the determination of thermal expansivities, compressibilities, and bulk moduli (as a function of pressure and temperature), as well as for thermodynamic calculations of all kinds.

#### Example 2: PVT studies of a solid

This example is taken from PVT work on polyimides [23]. The protocol was similar to that of the experiment in example 1, except that the samples remained solid (rather than liquid) throughout the study. This sample, which can not be



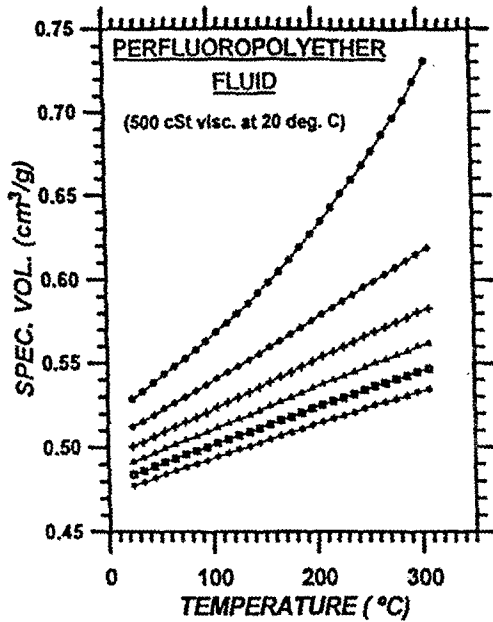


Fig. 1 PVT properties of a perfluoropolyether fluid (Krytox®, DuPont). Shown are cross-plotted isobars from 0 to 200 MPa in 40 MPa increments (top to bottom)

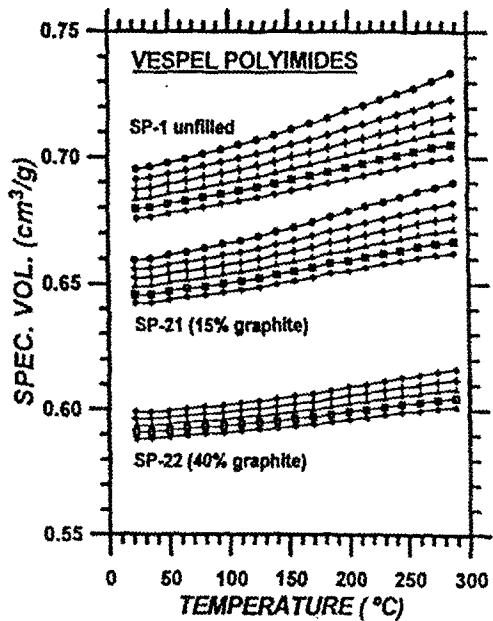


Fig. 2 PVT properties of solid polyimide polymers, with carbon content indicated (Vespel®, DuPont). Shown for each material are cross-plotted isobars from 0 to 200 MPa in 40 MPa increments (top to bottom)

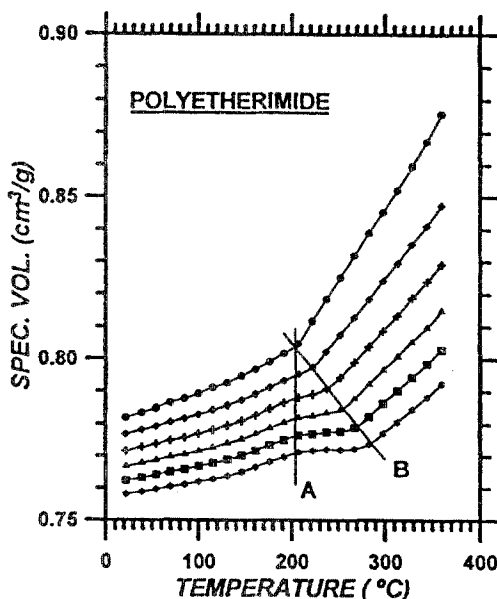
melted could not have been studied with the "piston-die" PVT technique at all. The results on three types of polyimides (Vespe<sup>l</sup>, DuPont) are presented in Fig. 2. The differences between an unfilled sample and two graphite containing samples are clearly visible. Both the thermal expansivity and the compressibility decrease as carbon is added, as one might expect.

Again, mathematical fits can easily be obtained to represent these data, and the effect of carbon filler can be modeled (although this is a rather complicated story, to be published elsewhere).

### Example 3: PVT behavior of an amorphous polymer

A sample of polyetherimide (Ultem<sup>®</sup>, General Electric) was chosen to illustrate amorphous behavior. Figure 3 shows some of the cross-plotted isobars, which were again obtained from data collected along isotherms, just as in the above examples. However, in this case, involving a glass transition, the mode of data collection becomes an important consideration in the interpretation of the results.

Turning our attention first to the zero pressure (atmospheric) isobar, a sharp break just above 200°C is clearly visible. This is, of course, the textbook appearance of a glass transition. Line A is an isotherm through the zero pressure



**Fig. 3** Characteristic PVT properties of an amorphous polymer (Ultem<sup>®</sup> polyetherimide, General Electric). Shown are cross-plotted isobars from 0 to 200 MPa in 40 MPa increments (top to bottom). Line A: isotherm through atmospheric-pressure glass-transition temperature. Line B: intersection of glassy isobars with melt isobars, yielding the pressure dependence of the glass transition (see text)

glass transition. Data to the left of line A belong to the PVT relationship of the particular glass that was placed in the PVT apparatus, reflecting the whole history that it had undergone since formation from a melt. Once measurements along an isotherm commence from the melt at 10 MPa, the sample will revert to a glass when a sufficient pressure is applied. However, the glass that is formed in situ in the apparatus in this way, is unlikely to be the same as the glass that was loaded in the apparatus, since it is formed under different conditions (at the very least at an elevated pressure). Thus, during measurements starting from the melt, a new glass with new properties is likely to be formed along each isotherm. This manifests itself in the densification observed between lines A and B in the plot. The densification is a dip to volumes lower than those expected by extrapolation of the data from the left of line A, which intersect the measured isobars roughly along line B. For isotherms entirely in the region to the right of line B, no glass transition is effected by the application of the maximum pressure of this measurements. Thus, points to the right of line B belong to the PVT relationship of the equilibrium melt. They can be fitted and thermodynamic calculations can be performed, just as they can on other liquids. Again, fitting theoretical equation of state to the data may provide scientific insight into the nature of the materials. This type of behavior is typical of all glass forming polymers, and has been discussed at great length.

In principle, then, it is possible to get precise data on thermal properties of glasses, with a certain formation history, the corresponding melt, and the pressure dependence of the glass transition (along line B), which usually is 30–60°C/100 MPa, playing a significant role in molding. There are many studies in the literature dealing with the glass transition under pressure. Representative examples from our lab are Ref.[24]: (four related polymers); Ref. [25] (compatible blends); and [26] (copolymers); these also contain numerous references to other work on amorphous polymers.

The study of glass-forming materials is not limited to the isothermal mode of measurement, but it is the method most easily and quickly applied. One can do direct isobaric heating and cooling experiments [27], and study the glass formation process by this method. It is even possible to study annealing of glasses by following the volume changes with time following pressure jumps in and out of the glassy state (to be published).

#### Example 4: PVT behavior of semi-crystalline polymer

Again, as in glass-forming polymers, crystallizable polymers present complications in PVT measurements in the form of a path dependence, which, however, afford opportunities for better understanding of polymers. We have recently discussed the PVT relationships of semi-crystalline polymers fairly extensively, and the reader is referred to this publication for additional detail

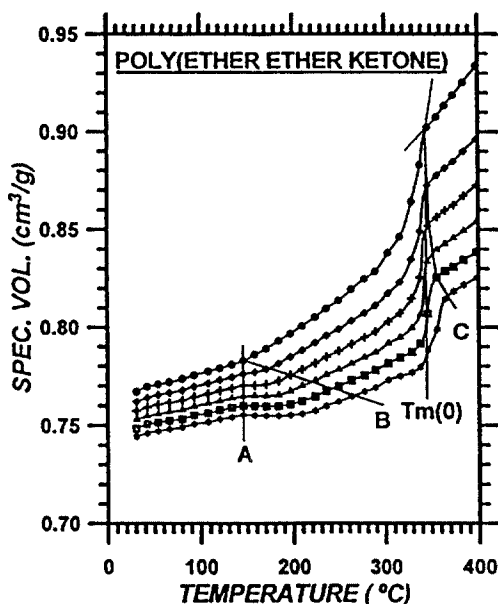


Fig. 4 Characteristic PVT properties of a semi-crystalline polymer, poly(ether ether ketone). Shown are cross-plotted isobars from 0 to 200 MPa in 40 MPa increments (top to bottom). Lines A, B: as in Fig. 3. Line C (onset of crystallization): see text

[8]. As PVT measurements commence in the solid state of a sample, formed by some previous process, the data represent the quasi-equilibrium PVT relationships of this particular structure. Now, as temperature and pressures change, the structure of a semi-crystalline sample may change, with accompanying volume changes. These volume changes, indicative of structural changes, although small, can be measured because of the absence of a base line problem in PVT measurements [8]. As temperature is increased, there comes the time when the sample goes through a melting process, usually easily visible by the large volume changes (5–15%) associated with it. An example of this is given in Fig. 4, based on cross-plotting isothermal data. The poly(ether ether ketone) polymer undergoes a glass transition in the vicinity of 150–160°C at atmospheric pressure. Just as in Fig. 3, A is a line through the zero-pressure glass transition temperature, and line B is the intersection of the isobars to the left of line A with the higher temperature isobars. Although this material is semi-crystalline in this temperature range, the glass transition is nevertheless clearly visible. Starting at perhaps 300°C the melting transition begins and ends at perhaps 338°C at zero pressure. Above this temperature, measurements along isotherms begin in the melt. Naturally, increasing the pressure would eventually produce re-crystallization, and this can sometimes be observed. The question is only this: will it

occur on the time scale of the experiment (about five minutes to reach the highest pressures), and to what extent? Thus, line C does not represent the pressure dependence of the melting point, but rather a line along which some crystallization begins to occur during the experiment. In order to measure the pressure dependence of the melting point (and the crystallization temperature on cooling at a certain rate) isobaric experiments need to be made [27]. For this material, the pressure dependence of the melting point was  $48.3^{\circ}\text{C}/100\text{ MPa}$ , and the pressure dependence of the onset of crystallization at a cooling rate of  $2.5^{\circ}\text{C min}^{-1}$  was  $51.2^{\circ}\text{C}/100\text{ MPa}$ . One finds that the pressure dependence of the melting point for semi-crystalline polymers is generally in the range of  $20\text{--}95^{\circ}\text{C}/100\text{ MPa}$  (see also below), and that, on cooling, the supercooling observed is often independent of pressure, but, of course, dependent on the cooling rate. It is also possible to use the pressure dependence of the melting point and the volume change between the melt and crystalline states at the melting point to calculate an independent value of the heat of fusion of the crystal, which is, of course, not amenable to direct measurement due to the semi-crystalline nature of polymers. For more details on the PVT behavior of PEEK, [27]; for a general discussion of all aspects of the PVT relationships of semi-crystalline polymers [8]. Of course one might also expect a dependence of the crystalline morphology (including "degree of crystallinity"), or even the crystal structure, on the pressure during crystallization. The most fundamental ways to study this is by determining the crystallization kinetics (and resulting products) as a function of pressure. We have made a start on this using PVT techniques at constant pressure and temperature, following the progress of crystallization by the associated volume change. We refer the reader to the relevant publications [28, 29].

### *High-pressure DTA measurements*

#### Calibration (and pressure dependence of the melting point of pure metals)

As is the case with atmospheric-pressure differential thermal analysis systems, the determination of the sample temperature needs to be done with great care, and involves occasional calibration. Basically three pure metals (lead, tin, indium, all of at least 99.99% purity) were used in developing calibration procedures. We did not assume a priori that anything was independent of pressure. However, after thorough work, the necessary calibration procedures for thermometric information turned out to be reasonably simple.

The sample temperature is calculated from the indication of the reference thermocouple (measured directly) by subtracting the differential temperature between reference and sample side. The thermometric sensitivity of the arrangement of differential thermocouples was determined by requiring each of

the three pure metals to melt at a single temperature at each pressure. There was an effect of scan rate on this sensitivity, no doubt reflecting a relatively large thermal resistance between thermocouple junction and sample. Remember: we use sheathed thermocouples and they must be ungrounded, adding to their thermal resistance. Fortunately this calibration can be done for all pressures at once, which is not surprising, since the thermal electromotive force of *K*-type thermocouples is effectively independent of pressure.

A further adjustment of sample temperatures was required to bring the zero-pressure melting points of the three pure metals mentioned in agreement with generally accepted values, viz. 156.6°C for In, 231.9°C for Sn, 327.5°C for Pb. This correction, fitted as a polynomial vs. temperature, could then be applied to the higher pressure results and led essentially to the correct pressure dependence of the melting points of these metals, as will be shown below. The sample size that needs to be used in this high pressure DTA is generally higher than that for atmospheric pressure machines. Masses as high as 100–200 mg were used for metals during calibration, 20–40 mg for polymers. This was necessary to get a strong signal, but also to substantially fill the Mettler pans, in order to prevent tearing of the pans under pressure, without the need to add inert substances (see above).

Figure 5 shows the signal for a tin sample as differential temperature vs. reference temperature at a scan rate of 7°C min<sup>-1</sup>, and a starting pressure of 150 MPa at room temperature. Melting begins at an (uncorrected) reference temperature of about 238.5°C. Along the front edge of the peak, the (uncorrected) sample temperature (=  $T_{ref}$  - diff. temp) remains essentially constant at this value. The pressure during the melting process has risen to about 155 MPa. A series of measurements at different scan speeds and pressures were performed and yielded essentially a straight line (see below). Individual data points

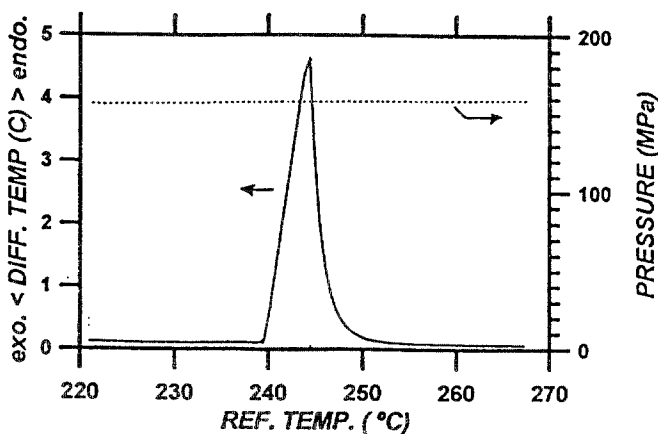


Fig. 5 Pressure thermogram of pure tin (heating: 7°C min<sup>-1</sup>)

in repeat experiment, with different sample masses, and at different scan rates can yield results that deviate as much as 1°C from this line. When a further correction is made, shifting the whole  $T_m$  vs.  $P$  lines to give the correct zero pressure melting point, the following values of  $dT_m/dP$  were obtained for the three calibrants, compared with literature values [30, 31]:

	$dT_m/dP$ (exp)/°C MPa <sup>-1</sup>	$dT_m/dP$ (literature)/°C MPa <sup>-1</sup>
Indium	0.0485	0.0492
Tin	0.0309	0.0344
Lead	0.0795	0.0755

Thus, there is reasonable agreement between our DTA results and literature values.

### Pressure dependence of the melting point of polymers

The high-pressure DTA technique was next applied to the determination of the pressure dependence of the melting point of several polymers. All these had previously been determined by PVT measurements, and comparisons between our high pressure DTA technique and PVT measurements are possible. Polymers inherently melt over a considerable pressure range, and the definition of the melting point becomes important. The most reasonable single melting point that can be quoted is probably the end of the melting interval, i.e. the point at which all the material has melted. The most perfect and largest crystals will

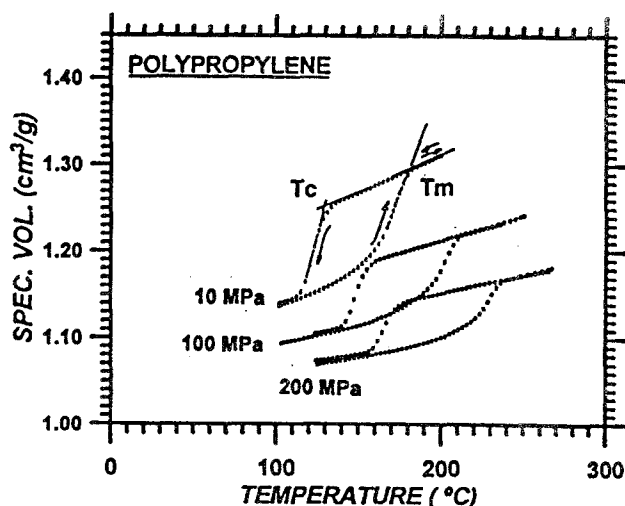


Fig. 6 Isobaric PVT runs on polypropylene at the pressures indicated, showing definition of melting points  $T_m$  and crystallization temperatures  $T_c$  from such experiments. Heating and cooling rate: 3°C min<sup>-1</sup>

melt last. In the PVT measurements the end of the melting interval is very sharply defined, as in Fig. 6, using polypropylene as an example [28, 29]. It is essential that each heating run, resulting in the melting point for a certain pressure, needs to be performed using an identical starting sample, with the same morphology, since the melting range of a polymer clearly depends on the morphology. This can be achieved by using a new sample for each run, or by preparing a sample in situ in the apparatus in an identical manner prior to each melting run.

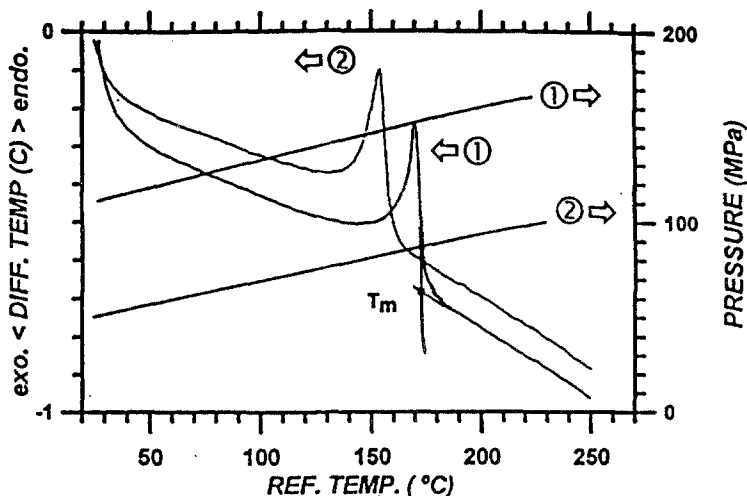


Fig. 7 Pressure thermograms of a polyethylene at two different pressures, indicating the definition of the melting point adopted (heating  $3^{\circ}\text{C min}^{-1}$ )

To compare PVT melting points with DTA melting points, the heating rates should be comparable as well ( $3^{\circ}\text{C min}^{-1}$  in this case), and a comparable definition of the melting point must be adopted. The heating rates should be comparable because the melting points of polymers actually can depend on heating rate, not because of some apparatus related effects – these are believed to have been taken care of. Figure 7 shows a melting peak of a 25 mg sample of polyethylene (not further characterized), including the definition of the DTA melting point adopted throughout this work. This definition of the melting point would certainly lead to an overestimation of the melting point in pure substances, and likely also in broadly melting substances, such as polymers – but it still seems to be the most reasonable procedure for the time being.

Figure 8 gives the results on a polypropylene (type 41E4 from Rexene Products Co.). It has an isotacticity greater than 96%, a number average molecular weight of 470000, and a weight average of 740000. For each DTA run, a new sample was used, cut from a molded disk of density  $0.906\text{ g cm}^{-3}$  at room tem-



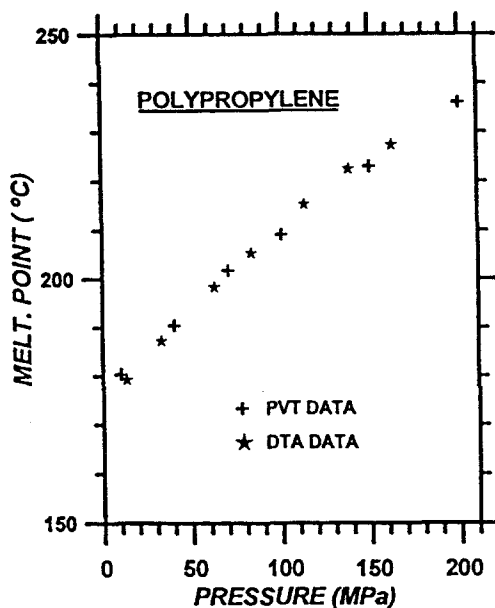


Fig. 8 DTA and PVT results of the dependence of the melting point of polypropylene on pressure. Heating rate  $3^{\circ}\text{C min}^{-1}$

perature. It is apparent in Fig. 8 that the PVT apparatus and the high-pressure DTA give similar results. Note that the pressure dependence of the melting point of polypropylene (and polymers in general) is much higher than that of metals. Another example is a relatively high molecular weight nylon 66 (DuPont Zytel 42) (Fig. 9). It had a number average molecular weight of about 27000 and a weight average of 58000. Samples were thoroughly dried, and had a density of  $1.143\text{ g cm}^{-3}$  at room temperature. Similar agreement between PVT and DTA techniques can be observed. If anything it might be observed that DTA melting points are somewhat higher than PVT melting points, perhaps because of the specific definition of the DTA melting point adopted (see above).

#### Limits of the current high pressure DTA technique

Attempts to measure the pressure dependence of glass transitions were modestly successful. Glass transitions can generally be detected, but they are not nearly as obvious as in conventional DTA techniques (or in PVT experiments, for that matter) because of the much reduced sensitivity of the high-pressure apparatus. A contributing difficulty is also a baseline, which is quite unreproducible, and often strongly curved. After data are recorded, a linear baseline with adjustable slope can be subtracted numerically from the thermogram. This

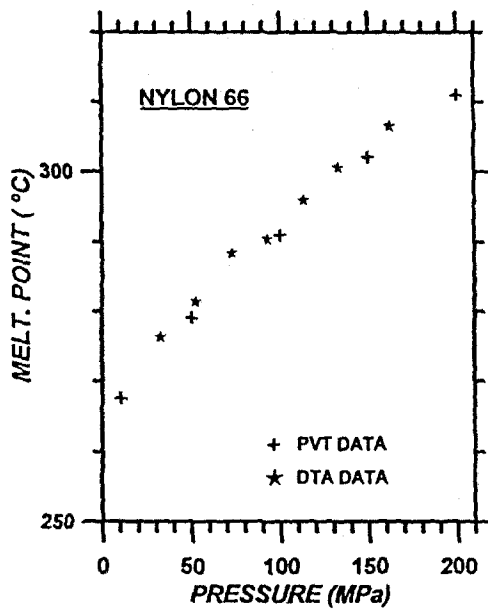


Fig. 9 DTA and PVT results of the dependence of the melting point of nylon 66 on pressure. Heating rate  $3^{\circ}\text{C min}^{-1}$

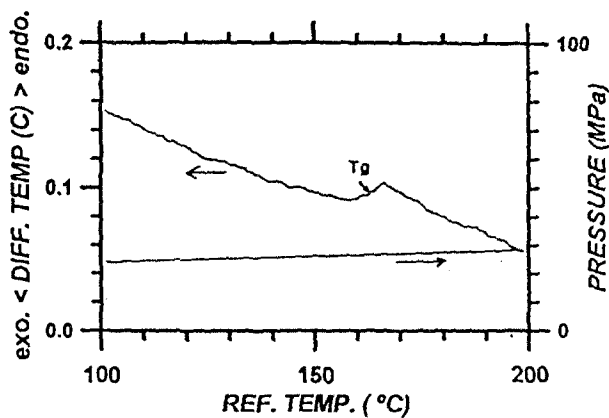


Fig. 10 Glass transition of polycarbonate in a pressure DTA run (heating  $3^{\circ}\text{C min}^{-1}$ )

normally makes a glass transition more obvious. An example of a glass transition is shown in Fig. 10 (polycarbonate).

Caloric information (heats of fusion, specific heats) can not be obtained at present because of the dependence of the thermal environment and thermal coupling on pressure, and because of the strong variability of the baseline. There is some hope that this may change sometimes in the future.

## Advantages and disadvantages of PVT and high-pressure DTA techniques

From a purely technical point of view we much prefer our PVT technique to our high-pressure DTA technique. The PVT technique is highly quantitative and (in addition to being able to measure equations of state), it can easily measure melting points, crystallization temperatures, glass transitions, and mesophase transitions as a function of pressure. In addition the techniques are sufficiently sensitive to test theoretical equations of state, mixing and de-mixing phenomena in blends or solutions, and a host of other phenomena. There are no baseline problems; the data are interpreted the same way by any scientist. The disadvantage of the PVT technique is clearly the effort required in acquiring data. While a modern PVT apparatus is completely automatic and is priced about the same as high-quality (atmospheric pressure) DTA system, the time required to measure data is longer, and there is more effort involved in mounting samples, and preparing for a new experiment in general.

There may thus be some room for doing high-pressure DTA experiments at present. With our system, results can be obtained on the pressure dependence of transition temperatures – certainly melting (see above) and crystallization, and also mesophase transitions in liquid crystal systems [33]. The glass transition can also be studied in most cases. This can be done with less experimental effort than the equivalent work using a PVT apparatus, but the results will be less precise. The experimental effort using a high-pressure DTA is however, still much higher than that involved in an atmospheric DTA or DSC apparatus.

Finally, one can wonder if enthalpic techniques and volumetric techniques will, where they overlap, always produce the same information, i.e. if enthalpy and volume play strictly equivalent roles. There are tantalizing indication that this may not be so. For example, Fakhreddine [32] in his work on thermotropic liquid crystal polymers did not observe nematic to crystalline transition peaks in a particular sample, neither by atmospheric pressure, nor by high-pressure DTA techniques, while such a transition was clearly evident using PVT techniques. This may be due to the easy interpretability and precision of PVT results (no baseline at all), but it may be indicative of a more profound distinction.

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