

**Jürgen Pionteck, Leibniz Institute of Polymer Research Dresden:
Characterization of polymer structure, transitions and reactions by PVT (Pressure-
volume-temperature) analysis**

1. Pressure-Volume-Temperature Data of Polymers

(NOTE: This text is slightly modified and taken from:

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1.1 Fundamentals for Understanding Macroscopic PVT Behaviour of Polymers

Pressure-Volume-Temperature (*PVT*) data of polymers are of practical relevance in technical applications and allow also insight in the thermodynamic behaviour of polymers under the influence of pressure and temperature and especially during phase transitions.

Typically *PVT* parameters are determined by measuring the specific volume, V_{sp} , in dependence on defined pressure, P , and temperature, T . Changing the PT parameters will cause changes in the V_{sp} value ($V_{sp} = f(P,T)$). Isothermic changes of the pressure are useful to determine the compressibility κ of polymers; isobaric changes can be used for the determination of the thermal expansivity α .

When one gives *PVT* data of polymers one has to decide in regard of equilibrium and non-equilibrium data. As long as the polymer is in the liquid, i.e. molten state, relaxation in polymers is fast and the measured data are equilibrium values.

On the other hand, below the glass transition polymeric materials become frozen and the relaxation processes may be too slow to follow changes of the outer conditions like pressure and temperature within a reasonable time and the measured values are non-equilibrium data. Even more complicate is the case of crystallisable polymers. Again, above the melting temperature T_m , which is generally above the glass transition temperature T_g , there is no problem with equilibrium conditions but in the solid, partial crystalline state a multiphase system is formed consisting of crystalline and amorphous phases. Both phases, the crystalline polymer and the amorphous, have different *PVT* characteristics. Above T_g the amorphous phase may be partial immobilized due to interaction with the neighbored rigid crystallites (the so-called “amorphous rigid phase”), another part may be mobile (“amorphous mobile phase”). Below T_g both amorphous phases are frozen, but still they react differently on changes of the PT parameter due to their different surroundings. In addition, the ratio between the phases is not constant and the crystalline phase of polymers itself can exhibit polymorphism, that means different crystal structures with different *PVT* properties. In the “quasi equilibrium state” the specific volume is constant with time since the kinetic of the transition from the non-equilibrium state to equilibrium is too slow to be measurable.

All these non-equilibrium states have some common characteristic: The measured specific volume depends not only on the P and T values, but on the way how the state was generated. The same set of PT parameters may result in very different specific volume. E.g., slow cooling will generate higher degree of crystallization than fast cooling. Increasing pressure will shift the glass transition and crystallization temperature to higher values and may cause even different crystallite morphologies.

On the other hand any process which causes changes in the chemical structure (degradation, crosslinking, transreactions) or morphology (melting and crystallization, crystal-crystal-transitions) will result in changes in the specific volume and their kinetics can be analysed by following the specific volume over time if the volume effect is big enough to be detectable with proper methods. From the technical point of view parameters like thermal expansion or compressibility and the knowledge of the specific volume itself are important for processing and application of polymeric materials.

This *PVT* behaviour of polymers in equilibrium can be well described by fitting the experimental data to a large variety of 2-dimensional or 3-dimensional (semi-) empirical equation-of-states (eos) models and theories. In common for all equation of states is that dimensionless variables of temperature, pressure and

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volume are obtained by dividing the real P , V , and T data by reducing parameters P^* , V^* , and T^* in the form of $\tilde{V} \equiv \frac{V}{V^*}$, $\tilde{T} \equiv \frac{T}{T^*}$, and $\tilde{P} \equiv \frac{P}{P^*}$. Overviews of reduced parameters and their underlying theories and approaches can be found in handbooks and reviews, e.g. [89Zol], [93Rod], [99Cho]. Reducing parameters have to be fitted in such a way that they give the best agreement between the model and the reality. Other approaches fit the molecular parameters of polymers and energy terms to different hard-sphere chain fluid models (HSCFs) based on the eos of Hu et al. [96Hu], [03Pen]. Group contribution approaches describe the PVT data on the basis of the chemical structure of the polymer units in combination with reducing parameters obtained from lattice fluid eos models (e.g. [00Bou]).

All the fitting procedures have the disadvantage, that they are only valid for equilibrium states and that the fitting result depends on the set of data points used. Changing the range will give different reducing parameters and recalculation of the PVT data from the fitted parameters will always cause some deviation from reality.

Of course also non-equilibrium data may be fitted to empirical equations but also these parameters depend on the history of the sample. Even eos theories have been used to fit such non-equilibrium states but the resulting parameters are thermodynamically meaningless.

1.2 Density, Specific Volume, and Methods for their Determination

Density and specific volume

Density ρ is the mass of a material in a unit volume and given in the unit g/cm^3 , kg/m^3 , or g/ml . The specific volume is the inverse of the density, $V_{\text{sp}} = 1/\rho$, with the unit cm^3/g (or m^3/kg or ml/g). The density of polymers at ambient conditions can be determined by different methods. For liquids pycnometers are favourable but also oscillation-type density meters can be used. For simple geometries the volume of bodies can be determined by measuring the dimensions and the density is then calculated from the weight to volume ratio. Density of solids of any shape can be determined by the density gradient technique using density gradient columns or by hydrostatic weighing applying the Archimedes principle. Mixed solvents can be prepared in such composition that the specimen floats without moving up or down and the density of the mixture can be determined pycnometrically or according to their composition/density correlation. The accuracy limit is given to be better than 0.2 % or even better than 0.05 %, depending on the method. Gas pycnometers, which work on the basis e.g. on helium displacement give accuracies as good as 0.03%. Each method has its advantages and for solid polymers most of the methods are suitable for samples in void-free form. Solids with very different shapes can be analysed (powders, films, granules, specimen of compact form) depending on the method applied.

Dilatometry

The knowledge of the volume or dimensions of a body is a prerequisite for dilatometry [86Zol], which concerns the measurement of dimensional or volume changes of matter. Depending on the needs, linear or volume changes can be determined with different techniques. In the easiest way the dimension changes are measured at constant pressure as function of temperature or time. For solids the isobaric linear thermal expansion coefficient α_L is defined as

$$\alpha_L = (1/L) / (dL/dT)_p \quad (1)$$

and the volumetric expansion coefficient α_v as

$$\alpha_v = (1/V) / (dV/dT)_p \quad (2)$$

with L = one dimensional length and V = volume of the sample.

For isotropic materials and small dimensional changes α_v equals 3 α_L .

Isothermal volume changes as result of pressure changes are given as compressibility κ in the form

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$$\kappa = -(1/V) / (dV/dP)_T \quad (3)$$

Both parameters are very important for technical processes.

Besides pressure and temperature, other stimuli causing dimensional changes are mechanical stresses, swelling, chemical reactions like polymerization, crosslinking, transreactions or degradation, aging, crystallization, melting, isotropisation, or glass transition. In general, all processes causing dimension changes including void formation, foaming or craze formation due to mechanical stress can be analysed by dilatometry.

Linear dilatometry

Dilatometers measuring linear dimensional changes on solids are working normally at standard pressure. For isotropic materials the one-dimensional determination of the length change is sufficient, but for anisotropic materials like uniaxial reinforced polymers or highly oriented polymers the dimensional changes have to be measured in all three or in two directions.

Thermo-mechanical analysis delivers directly thermal expansion coefficients and is useful also for analysis of phase transitions like glass transition temperature. The dimension change of the object to be studied is analysed by an external very precise LVDT (linear variable differential transducer) unit, which is connected to the sample by a rod. The LVDT unit ensures high accuracy in dimension determination of better than 0.1 %. However, it measures in one dimension and in contact mode that means a marginal force is acting on the sample, which may cause problems in case of soft, easy deformable materials. Other instruments use electrical slide wires, capacitive gauges or mechanical-dial indicators for analysing the dimension change. For very low changes in length optical interferometry may be used. For even better accuracies high resolution laser dilatometer can be used. Optical dilatometers measure dimensional changes in a non-contact mode and in all dimensions.

Volume dilatometry

Volume dilatometry is useful to determine changes in the volume of liquids or solids in dependence on outer stimuli (temperature, pressure) or as function of time. In the simplest way a reservoir of known dimension of a liquid is connected with a precise calibrated capillary, similar as it is in a mercury thermometer, and the change of the volume of the liquid can be read on the scale of the capillary. Such system measures not the volume of the liquid directly but its changes, δV . For determination of the actual volume of the sample, V at known conditions (T , P) has to be determined separately with methods described above. Since the reservoir volume also will change due to temperature changes the whole system must be calibrated to the temperature change and the capillary volume must be small compared to the reservoir.

The same construction can be used for determination of volume changes of solids or liquids applying the confining fluid technique. Typically mercury is used as confining liquid (mercury dilatometer) and the whole dilatometer is calibrated against temperature changes by performing a temperature run of the system completely filled with the confining liquid. When a part of the confining liquid in the reservoir is substituted by the second component, the volume change of this component can be calculated from the combined measured volume change, when the expansion properties of the confining liquid are known. Of course, no reactions between the two substances should occur and the substances must be strictly immiscible or insoluble in the confining liquid. These conditions are given for almost any polymer in combination with mercury as confining liquid.

To analyse the pressure influence on the volume expansion behaviour the whole mercury dilatometer may be enclosed in a pressure vessel [97Sat]. However, more comfortable are bellows-type dilatometers, which measure directly volume changes of a substance as a function of temperature, pressure, and time. Fluids can be measured directly or, like solids, applying the confining fluid technique ([86Zol], [95Zol]). The material to be analysed, with or without confining fluid, is filled in a cell of a defined volume, which is closed at one end by a movable bellow. Any volume change of the completely filled cell is recorded by deflection of the bellow, which is connected with a measuring unit by a stiff rod to determine the exact position of the bellow. The volume change is than the bellow shift multiplied by the bellow cross-sectional area. Again, also the volume of the cell will be dependent on the pressure and temperature, and

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the system has to be calibrated over the whole temperature and pressure range using a liquid with known *PVT* parameters. Typically mercury is used for calibration and as confining fluid. For conversion of the measured volume change to the actual volume, V of the material at defined conditions, typically near to room temperature and at ambient pressure, has to be determined externally.

Dilatometers of the cylinder-piston type are useful for determination of *PVT* data of viscous liquids like polymer melts or liquid polymers. A cylinder of defined diameter is closed at one end with a movable piston and the volume of the sample filled into the cylinder can be calculated directly from the position of the piston, i.e. its distance to the cylinder bottom. If the material expands or shrinks the piston keeping a defined pressure on the sample will follow the changes and its throw will be measured by typical methods described above for linear dilatometers. Again, the cylinder diameter will be affected by T and P changes and a calibration of actual cell volume is necessary. Compared to the confining fluid dilatometers the main problem of cylinder-piston type dilatometers is the possible leakage of material at the piston end which would pretend volume changes and, therefore, have strictly to be excluded. Otherwise the friction between piston and cylinder must be low enough that the pressure acting on the piston is completely transmitted onto the sample to be analysed.

1.3 The GNOMIX *PVT* Apparatus

If not other mentioned all data were determined by means of the GNOMIX *PVT* high pressure dilatometer (GNOMIX, Inc., 3809 Birchwood Drive, Boulder, CO 80304, USA) [91Fak], [95Zol]. A schematic image of the apparatus is given in Figure 1.1. The principle of the GNOMIX-*PVT* apparatus is the confining fluid technique. In this technique the material studied is surrounded by a confining fluid, which ensures that the material is under hydrostatic pressure at all times. The apparatus is able to collect *PVT* data in the range from 10 MPa to 200 MPa in increments of 10 MPa, and from room temperature up to 400 °C.

In the isothermal standard (ITS) mode, after reaching thermal equilibrium, the pressure is raised from 10 to 200 MPa and all data are recorded in steps of 10 MPa. Then the material is depressurised to 10 MPa and after reaching the equilibrium of the next desired temperature the next ITS run starts. In this way the T -range from RT to 400°C can be analysed. The values for 0 MPa (actually the value for atmospheric pressure) are obtained by extrapolation of the values for 10 MPa to 30 MPa in steps of 1 MPa according to the TAIT equation (see [89Zol], [95Zol]) for each temperature using the standard *PVT* software.

In the isobaric mode (IBA) the sample will be heated or cooled at defined rate and defined pressure. Phase transitions can be easily detected in this mode.

In a special (data acquisition, DAQ) mode it is possible to follow changes of the specific volume at constant pressure and constant temperature, which may be caused by a phase transition, e. g. [94He]. While the accuracy limit for the absolute values of the specific volume is within 0.002 cm³/g (above 240°C 0.004 cm³/g), volume changes as small as 0.0002 cm³/g can be resolved reliably. For the measurements mercury is used as the confining fluid. About 1.5 mL of the material embedded in a nickel foil sample cup is used for the *PVT* studies. The nickel cup ensures that the material does not stick to the wall of the cell and that at all times the hydrostatic pressure is maintained on the sample [92He]. The overall volume of the sample cell is about 7.1 cm³.

Since the apparatus detects not the absolute specific volumes but its changes in dependence on P , T and time t the so-called additional volume V_{add} has to be added to the dV_{sp} values to obtain the actual specific volume $V_{\text{sp}(T,P)}$. Usually, V_{add} is determined for standard conditions at $P = 0.1$ MPa and at 25 °C by any method given above. In cases where no density data are available the material density can be determined from the *PVT* cell filling procedure, knowing the exact cell volume, the mass of all components filled into the cell, and the densities of the Ni cup and mercury. The accuracy is usually within 0.5 %, estimated from comparison with helium pycnometer data. Thus, the accuracy of the given values depends also on the accuracy of the method used for the determination of V_{add} . Furthermore, no volatile components should be present in the material to be analysed (the cell containing the sample is for filling with mercury evacuated to a vacuum of 0.0002 torr) and it should not react with mercury or stainless steel.

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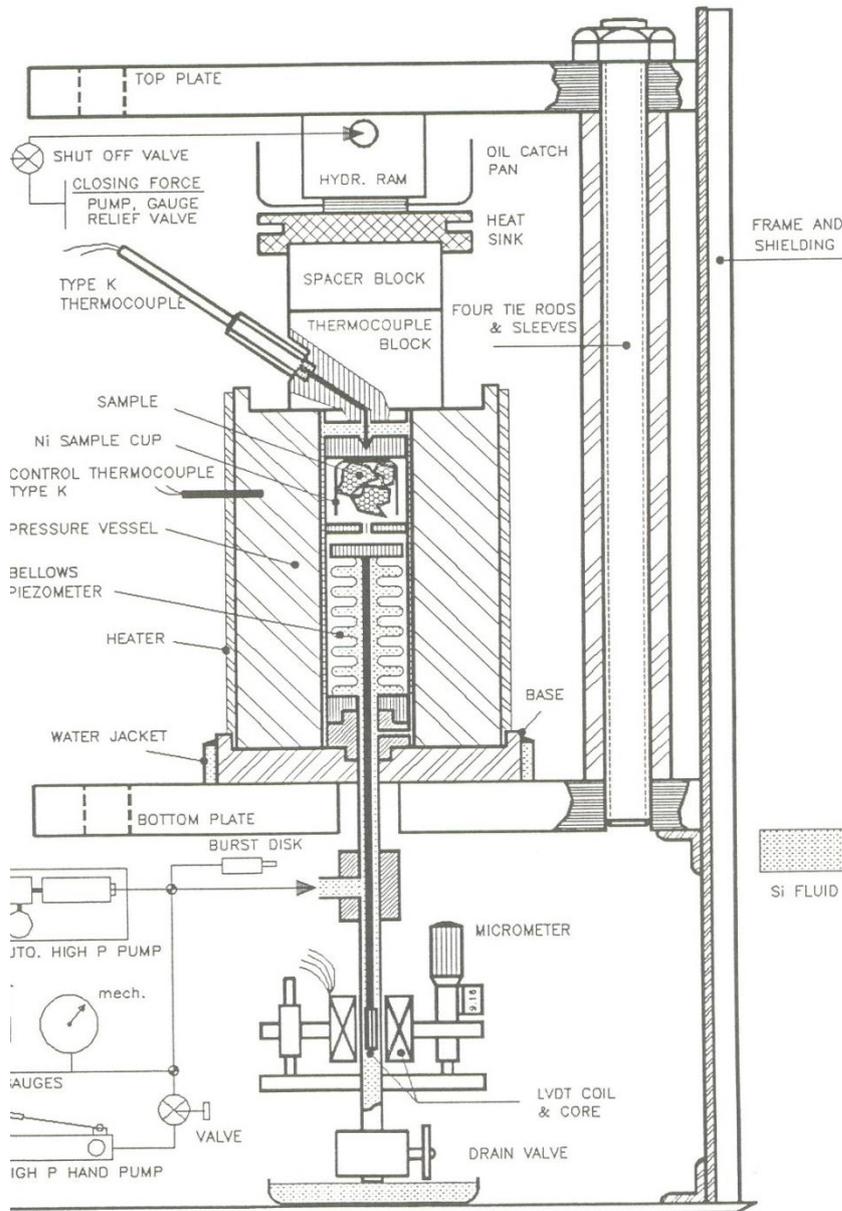


Fig. 1.1: Scheme of the GNOMIX PVT Apparatus

Typical ITS runs are shown in the Figure 1. Poly(isobutylene) shows no phase transition, the isobars drawn from the ITS runs are nearly linear. Polycarbonate shows a glass transition, detectable as a change in the slope of the V_T dependency. Polyethylene shows a melting transition, resulting in a step-like increase of V_{sp} in dependence on T . In Fig. 1.2 the open symbols mark the range of stable conditions (equilibrium – above the transition temperature range; pseudo-equilibrium below this range), while the solid symbols mark instable conditions, where during the pressurization phase transition occurs.

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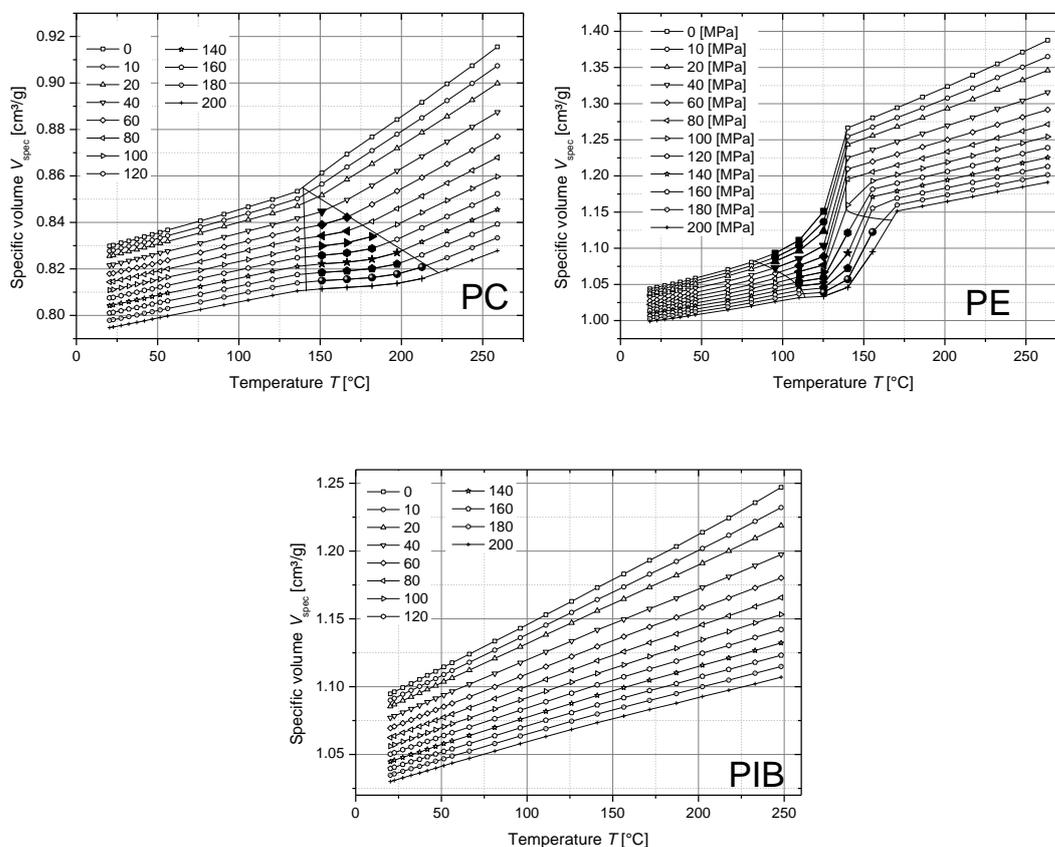


Fig. 1.2: Typical PVT behaviour of polymers showing glass transition (polycarbonate, PC Lexan 121), melting (poly(ethylene), PE-HD 25055E), or being in the liquid amorphous state in the whole measuring range (poly(isobutylene), PIB, laboratory grade). The open symbols characterise the stable quasi-equilibrium or equilibrium state of the polymers, the solid symbols the transition ranges. The regions are separated by lines to guide the eyes [own results].

1.4 References for 1

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2. Samples for PVT Analyses of

(Note: The samples given here are own results. In case that they have been published, in this or in a modified form, the citations are given)

UHMW PE - 598

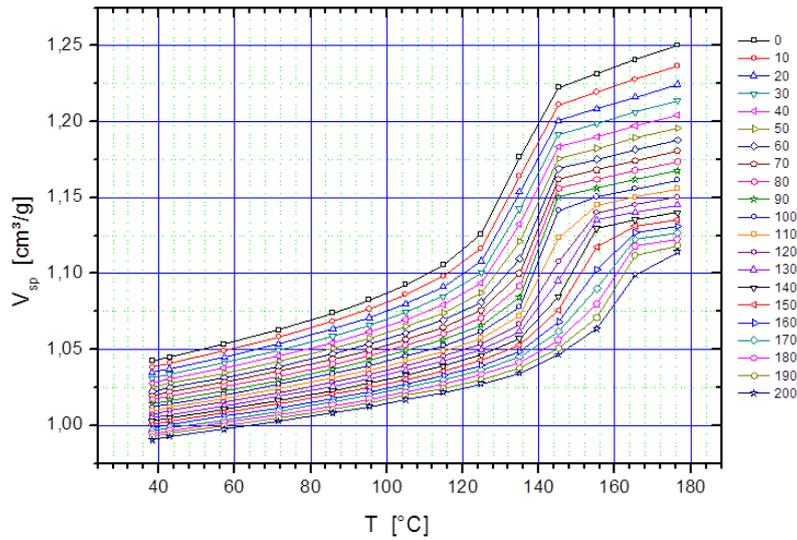


Fig. 2.1: Melting of UHMW PE, ITS runs [14Pio]

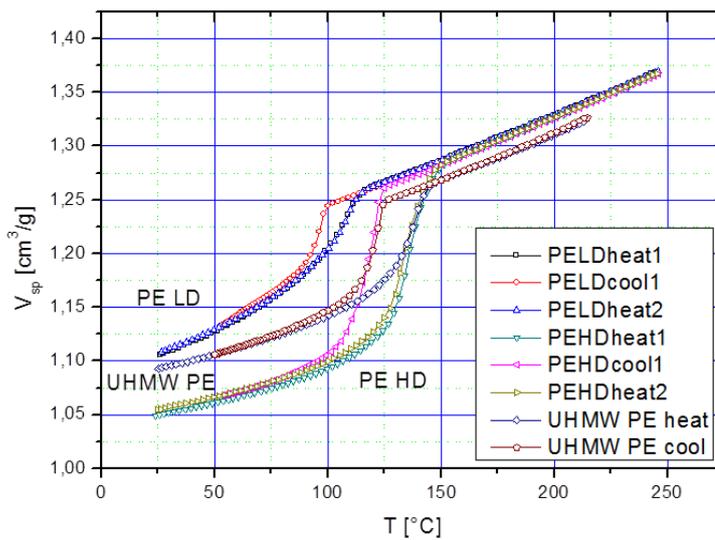


Fig. 2.2: Influence of chain branching on T_m and V_{sp} of different PE (IBA runs).

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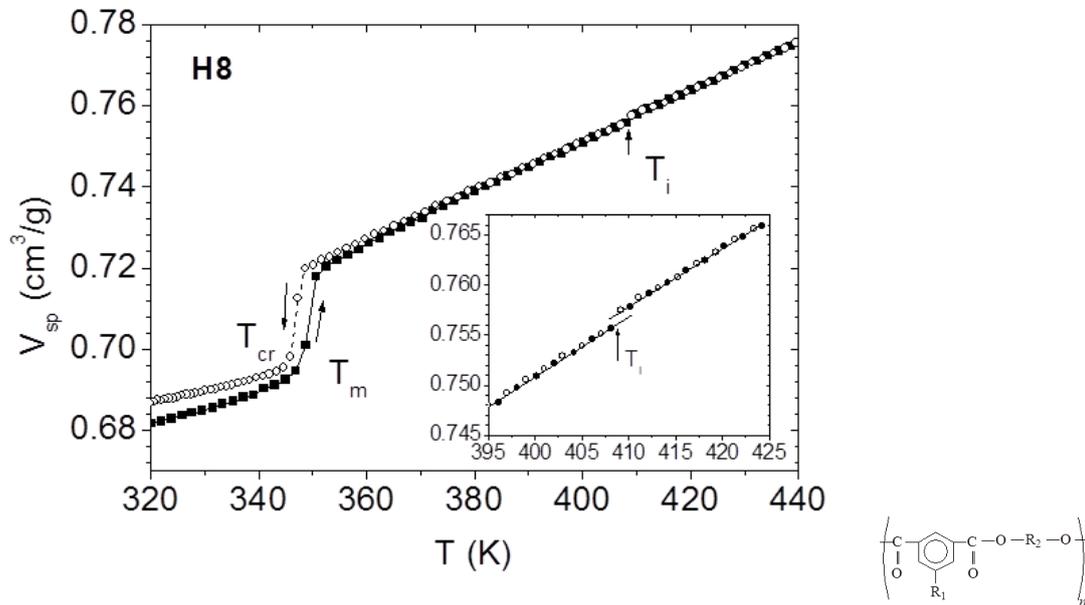


Fig. 2.3: Crystallisation and isotropisation of a semifluorinated polyester, IBA [02Got]

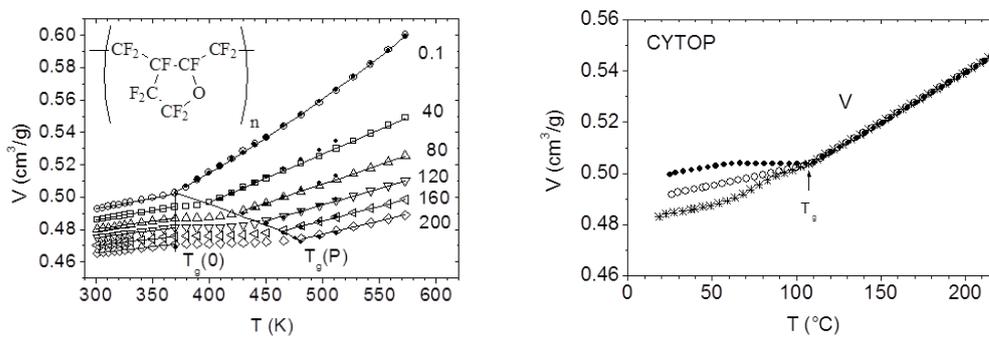


Fig. 2.4: Influence of history of treatment on V_{sp} values of CYTOP; left ITS virgin CYTOP, right IBA 10 MPa; open symbols: virgin; filled symbols: CO_2 -swollen, stars: pressure densified [07Dlu], [08Dlu]

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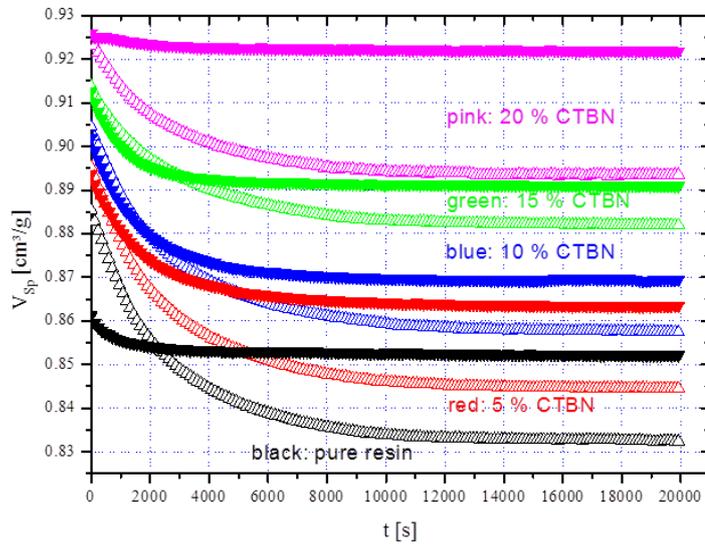


Fig. 2.5: Influence of rubber reactivity onto cure shrinkage of epoxy resin, DAQ run [07Mül]

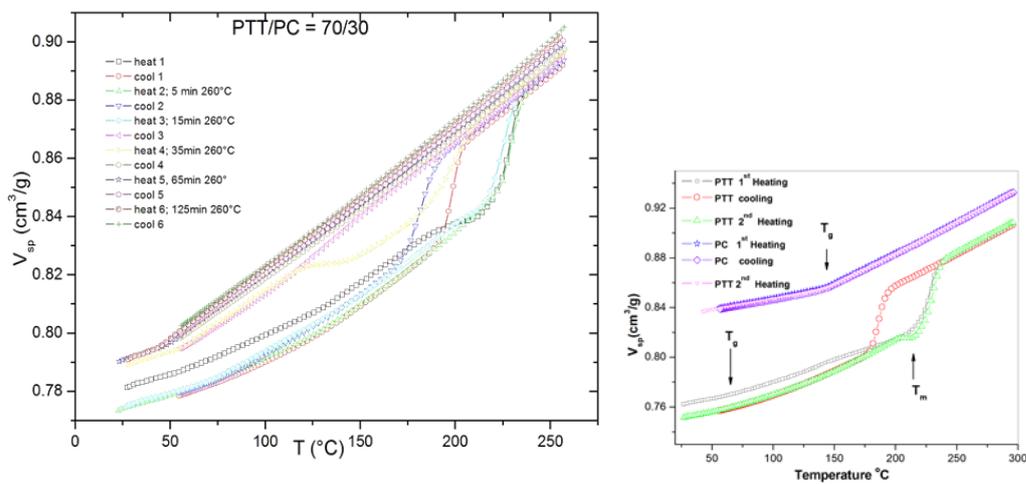


Fig. 2.6: Changes in glass transition, melting and crystallization, and specific volume due to trans-crystallisation of PTT/PC blends, repeated IBA runs (the right images shows the behavior of the pure materials) [12Ara]

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