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The Use of Pressure-Volume-Temperature Measurements in Polymer Science

Dedicated to Prof. *Jung-Il Jin*, Korea University, Seoul, on the occasion of his 60th birthday

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Summary: The importance of the knowledge of thermodynamic parameters from p-V-T experiments is shown in different fields of polymer science with special emphasis on determination of the phase behaviour of polymer systems.

Keywords: phase behavior; thermodynamics

Introduction

Physical chemistry describes the state of a system regardless of its shape size and constituents by variables of state like pressure p, thermodynamic temperature T, volume V and composition. The composition of a condensed material is usually given, e.g., as molar concentration c_i [$\mathrm{mol \cdot L^{-1}}$], molal concentration m_i [$\mathrm{mol \cdot kg^{-1}}$], molar fraction x_i, mass fraction χ_i, or volume fraction φ_i. The volume is sometimes normalized to the molar volume $\overline{V}$ [$\mathrm{cm^3 \cdot mol^{-1}}$] or the specific volume V_{spec} [$\mathrm{cm^3 \cdot g^{-1}}$], which is identical with the reciprocal density ρ^{-1} [$\mathrm{m^3 \cdot kg^{-1}}$]. The variables of state are correlated by appropriate equations of state (EOS). A well-known example is the equation of state of an ideal gas

$$p \cdot V = n \cdot R \cdot T \tag{1}$$

$$R = N_L \cdot k_b = 8,31451\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \tag{2}$$

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$p \equiv$ pressure [Pa], $V \equiv$ volume [m^3], $n_i \equiv$ amount of substance component i [mol], $R \equiv$ gas constant, $T \equiv$ thermodynamic temperature [K], $N_A \equiv$ Avogadro's constant ($6.022 \cdot 10^{23}$ mol^{-1}), $k_b \equiv$ Boltzmann's constant ($1.38066 \cdot 10^{23}$ $J \cdot K^{-1}$).

In liquid and solid systems it is convenient to use reduced variables (indicated by ~) and reducing, characteristic values (indicated by *). The characteristic terms T*, p* and V* are correlated with molecular structures, as shown below, Equation (11) - (14).

There are extensive variables (respectively extensive equations of state) – like volume or mass (entropy S or internal energy U) – which depend on the amount of material and intensive variables (respectively intensive equations of state) – which do not depend on the amount of material – like pressure, temperature or concentration (molar entropy or density). A simple fictive experiment discriminates between the two types of physical entities: divide the system, if the variable or equation behaves correspondingly, the entity was an extensive one, if it remains unchanged it is an intensive entity.

In case of a pure substance the variables p, V and T are frequently used while in multicomponent systems the composition has to be taken into consideration, so that the state Z of a particular system consisting of i independent components can be described by a general equation of state $Z(p, \upsilon, T, n_i)$ with the corresponding total differential

$$dZ = \left(\frac{\partial Z}{\partial V}\right)_{T,n_i} dV + \left(\frac{\partial Z}{\partial T}\right)_{V,n_i} dT + \sum_i \left(\frac{\partial Z}{\partial n_i}\right)_{V,T,n_{j\neq i}} dn_i \qquad (3a)$$

$$dZ = \left(\frac{\partial Z}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial Z}{\partial T}\right)_{p,n_i} dT + \sum_i \left(\frac{\partial Z}{\partial n_i}\right)_{T,p,n_{j\neq i}} dn_i \qquad (3b)$$

Usually, some of the variables are held constant during experiments so that Equation 3 becomes more simple. Many physico-chemical experiments are carried out isothermally, isobarically or at constant volume without chemical reactions. Many chemical reactions are carried out at constant temperature (i e in a boiling solvent) and at constant pressure (ambient pressure).

The partial derivatives of the different fundamental equations of state are frequently easy to obtain experimentally or can be calculated by the Maxwell-relations. For the condensed materials the partial derivatives:

heat capacity at constant pressure $$c_p=\left(\frac{\partial H}{\partial T}\right)_{p,n_i} \tag{4}$$

heat capacity at constant volume $$c_V=\left(\frac{\partial U}{\partial T}\right)_{V,n_i} \tag{5}$$

coefficient of isobaric expansivity $$\alpha = \frac{1}{V_o}\left(\frac{\partial V}{\partial T}\right)_{p,n_i} \tag{6}$$

coefficient of isothermal compressibility $$\kappa = -\frac{1}{V_o}\left(\frac{\partial V}{\partial p}\right)_{T,n_i} \tag{7}$$

are of particular interest concerning processability, miscibility, phase transitions, and surface properties of polymeric materials. V_o is the initial volume of the sample, the individual partial differential quotients are called expansivity and compressibility, respectively. Heat capacities are easily accessible by calorimetric measurement, α and κ can be obtained by p-V-T-experiments. Application of Euler's chain law finally yields:

$$\left(\frac{\partial p}{\partial T}\right)_{V,ni} = -\frac{\left(\frac{\partial V}{\partial T}\right)_{p,ni}}{\left(\frac{\partial V}{\partial p}\right)_{T,ni}} \tag{8}$$

Thermodynamic data like these and the knowledge of an appropriate equation of state are extremely useful and frequently underestimated.

A typical p-V-T experiment showing different possible transitions – including mesophase transitions is shown in Figure 1. In liquids it is frequently observed that the function V(T) is approximately linear over a rather broad range which means that α is constant. This linearity is, however, only observed when the system rests in internal equilibrium. If a glassy transition occurs or dissolved gas is liberated a sharp deviation from the linearity (a bend in the curve) is observed.

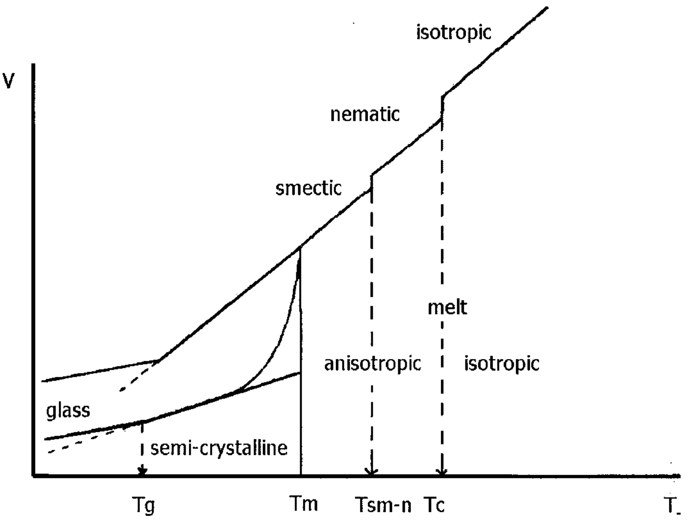

Figure 1. Schematic p-V-T diagram of an amorphous and a semi-crystalline substance, respectively, showing a glass transition and several first order (mesophase) transitions. Beyond the melting transition Tm the system obtains an (anisotropic) liquid crystalline state and the isotropic molten state at the clearing temperature Tc

Experimental Technique

There are two principally different methods of performing p-V-T measurements. The first method encloses the sample in a cylinder where the pressure is applied by a piston[1, 2, 3]. Since any leakage has to be avoided, it is necessary that cylinder and piston must fit as good as 10^{-4} cm over the whole pressure and temperature range. This method only provides a hydrostatic-type pressure equal from all sides to liquid samples and gases. The volume changes are calculated from the piston displacement. The second method has the sample in a pressure cell confined by a fluid – usually mercury. This provides an allround hydrostatic pressure to all types of samples, even for glassy and crystalline samples. Changes of the specific volume are determined from the combined changes of sample and confining fluid, usually monitored by the longitudinal displacement of a metal bellows. A commercial available equipment developed and produced by Gnomix® (P. Zoller) Boulder, Colorado, U.S.A., basing on the second principle is shown in Figure 2 and extensively described by Zoller.[4]

The external pressure is applied to a rigid sample cell, containing sample and confining fluid, which is connected to a flexible bellows. The bellows adjusts its volume according to the pressure applied by an external pressure line operated with a high-temperature stable silicone oil. The sample cell itself is surrounded by a solid, temperature adjustable pressure cell. The measuring range is from ambient temperatures to about 350°C, only limited by the boiling point of the confining fluid, and from 10 MPa to 200 MPa with an accuracy better than $2 \cdot 10^{-3}$ cm^3 g^{-1}. Zero-pressure values are obtained by extrapolation. The usual mode is isothermal, that means that the sample is set to a certain temperature and the pressure is increased in well defined, programmed steps to the end-temperature from where it goes back again to the starting temperature. The next temperature is then obtained and the pressure cycle is started again. A typical pressure step width is, e g, 10 MPa. The measuring frequency can be so small that the values often come close to equilibrium values. Typical rates for a temperature change are about 15 K/20 min and from ambient pressure to 200 MPa with a reading every 10 Mpa. A typical rate for the pressure change is 200 Mpa/5 min. The linear volume change of the bellows is measured through the displacement of a linear variable differential transformer (LVDT). The off-zero values of the LVDT are directly used for determination of the volume change with an accuracy of $10^{-3}cm^3$. Isobaric experiments are also possible. The isotherms with p equal to zero are obtained by extrapolation. Near transitions it can take some more time to obtain a constant reading.

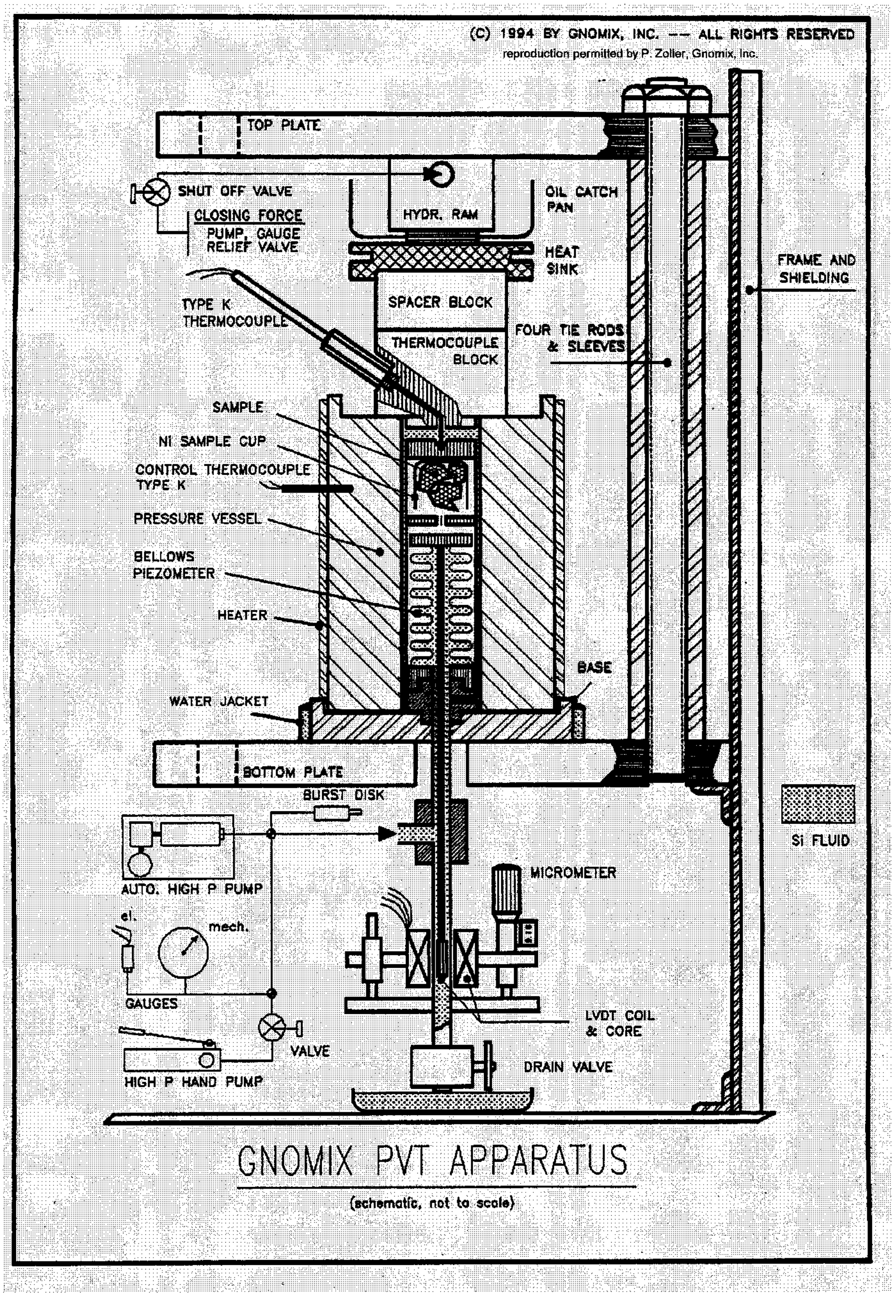

Figure 2. Schematic representation of a Gnomix® machine, Gnomix Research, Boulder Coplorado, U. S. A., for p-V-T measurements. Reproduced with the permission of P. Zoller, Boulder Colorado. For details see text and the corresponding publications by P. Zoller, e.g. [4] or others by this author

Applications

p-V-T relationships in polymer solids and melts are still underestimated in their value in materials science. The data can be extremely useful in at least five major areas, such as:

- Optimizing processing parameters[a] instead of establishing such parameters by trial and error;
- Prediction of polymer-polymer miscibility;
- Correlation of the reducing parameters of equations of state (EOS) with molecular structures;
- Prediction of service performance and service life of polymeric materials and components on the basis of free volume concepts;
- Calculating of surface tension of polymer melts;
- Evaluation of start and progress of chemical reactions in polymer melts in cases when volume effects accompany the reaction;
- Materials properties of systems in contact with solvents or gases;
- Investigation of the nature of phase transitions

In the injection moulding process time and path dependence of the specific volume, phase transitions and miscibiltiy behaviour of blends play a major role during the solidification process of the molded part. If this behaviour can be simulated in a small-scale equipment, much time, material and money can be saved.[a] Menges[5, 6] and his group have designed a corresponding equipment. If material is processed which can show (different types of) mesophases, see Figure 1, the knowledge of the conditions for their existence is crucial. In some cases, however, the slow cooling rate given by the high mass of the pressure vessel, see Figure 2, may be of some disadvantage.

Polymer-polymer miscibility is governed by the Gibbs energy of mixing. It can be related to the differences between the expansivities of the components and can be described largely on the basis of free volume statistical mechanical theory of Flory and others.[7, 8, 9, 10] A low free volume means a low expansivity and a high value of the reducing temperature T*, see below. Brostow and coworkers,[11] for example, found that V* goes symbatically with the length of

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[a] However, the time scale of the experimental conditions frequently differ significantly from the conditions in e g an injection moulding machine. Nevertheless many important and valuable information can be drawn from conventional p-V-T-experiments.

soft segments in polyurethanes while T* decreases with the length of the soft segments because of the corresponding weakening of interchenar interactions. For further details see also the review of Olabisi[12] and Sanchez.[13] The chemical potentials μ_i of the individual components can be derived from the reducing parameters* of an EOS, and the polymer-polymer interaction parameter χ_{23} is given in the simplest possible case by a rather crude approximation for non-polar systems:

$$\chi_{23} = p_1^* + p_2^* - 2(p_1^* \cdot p_2^*)^{1/2} \tag{9}$$

Only small differences – such as ~8 J·cm^{-3} in p* and ~190K in T* - can determine miscibility or immiscibility. However, the reduced pressure seems to be the more important value.[14] Figure 3 shows the isobars near the melting transition of a low density polyethylene, LDPE. Figure 4 shows the glass transition of a miscible blend.

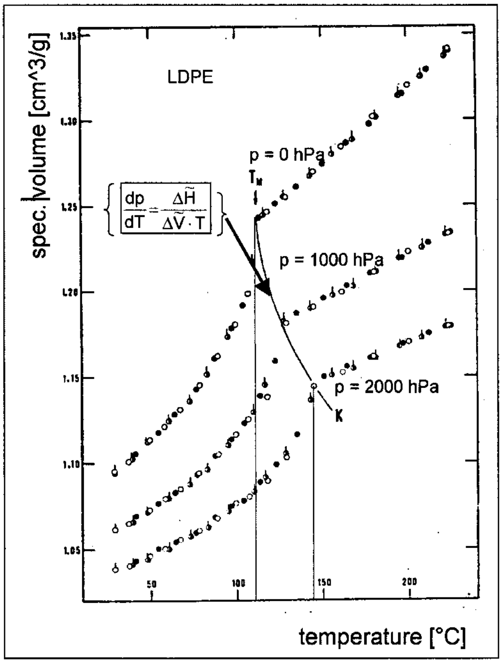


Figure 3. The melting transition of a LDPE at three different pressures after P. Zoller[15]

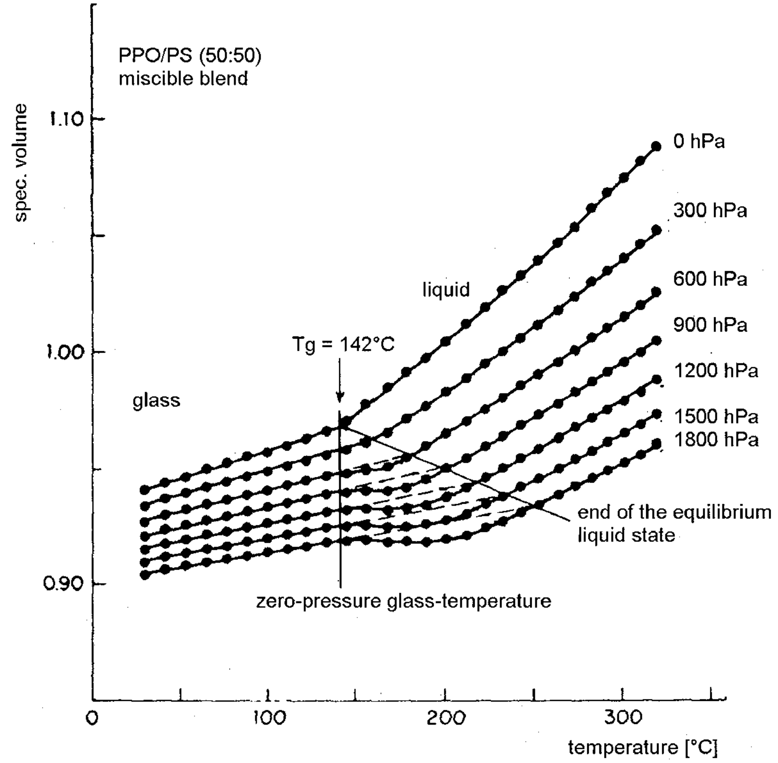


Figure 4. Pressure-dependence of the (single) glass transition of a miscible blend PPO/PS (50:50), after Zoller and Hoehn[16]

The correlation of phenomena in a p-V-T (isobaric) diagram is shown in Figure 5 with an example of a polymer liquid crystal, which has been investigated by Frenzel.[17]

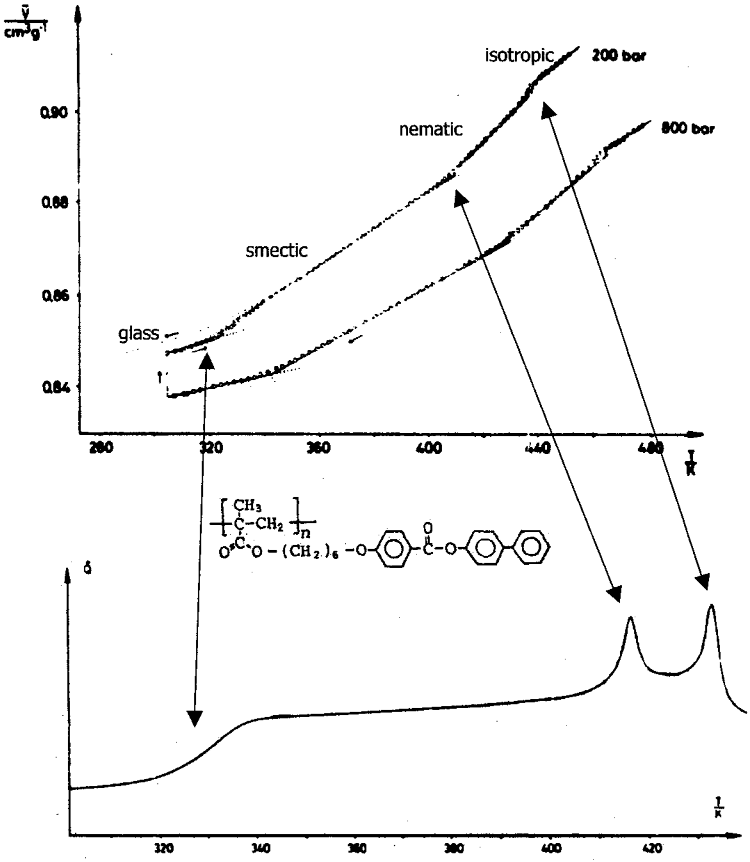


Figure 5. Phase transitions in a polymer liquid crystal p-V-T-measurement (top) compared with differential scanning calorimetry (DSC) (bottom) after Frenzel [17]

The free volume concept is very important for the interpretation of many polymer properties, see, e g, Ferry,[18] Simha,[19] Flory[20, 21] and others.[22, 23, 24, 25] Simha once stated: "if there was no 'free volume' it has to be invented".[26] The free volume V^f is defined by:

$$V \equiv V^* + V^f \tag{10}$$

with V^f ≡ free volume and V^* ≡ the characteristic volume for a given equation of state. Positron annihilation measurements can give an estimate of V^f. V^* is also sometimes called the 'net volume'[27] or the hard-core volume[28, 8, 29]. Hence, V^* can be interpreted as the volume that is left after the free volume has been squeezed out of a system. The free volume depends on temperature, pressure, stress level in tension, compression, shear, bending etc, and frequency in oscillatory experiments. The term:

$$\tilde{V} \equiv \frac{V}{V^*} \tag{11}$$

is called reduced volume. Reduced values, indicated by the tilde (~) and characteristic values, indicated by *, occur in equations of state (EOS). Important values are the reduced pressure $\tilde{p}$ and the reduced temperature $\tilde{T}$, normalized correspondingly to Equation (11). The physical meaning of the characteristic (reducing) values p^* and T^* are not as "simple" as the interpretation of V^* and may differ in the different theories. In terms of Hartmann's approach with

$$\tilde{p} \cdot \tilde{V}^5 = \tilde{T}^{1.5} - \ln \tilde{V} \tag{12}$$

p^* is given by:

$$p^* = \frac{2\pi}{9\mu}\frac{N}{V} r \frac{d(u)r}{dr} g(r) \tag{13}$$

$\frac{N}{V}$ is the number of segments per unit volume, μ is a geometrical factor depending on the coordination number z ($z = 6 \rightarrow \mu = 1$), u(r) is the interaction potential, and g(r) is the binary radial distribution function with the average segment distance r.

$$T^* = \frac{3(z-2)\varepsilon^*}{k} \tag{14}$$

ε^* is the intersegmental potential energy minimum, hence T* is high when the intersegmental interactions are strong. k is the Boltzmann constant. Figure 6 shows an example of the description of a series of polymers with the Hartmann equation.

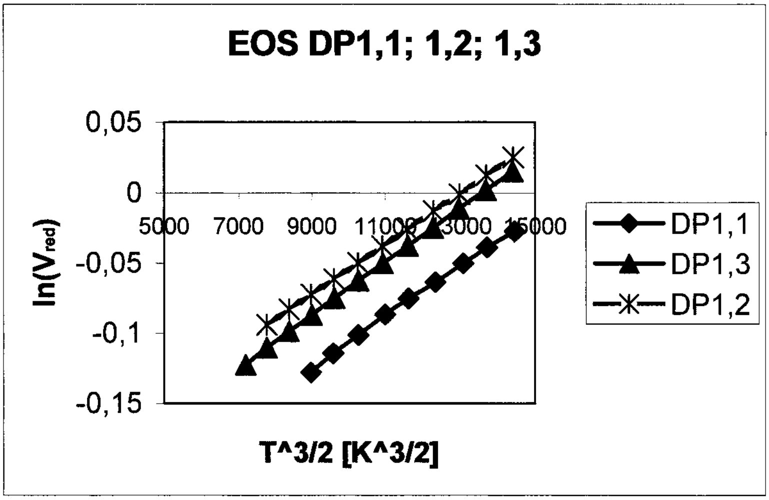


Figure 6. The polymers DP 1,1, DP 1,2 and DP 1,3 (the structure of the molecules is given in Figure 7, the number gives the number of carbons in R1 and R2, respectively) can be described in the fluid state by the Hartmann equation, Equation (12). The "wiggles" in the graph of DP 1,1 reflect mesophase transitions which are different and much weaker in DP 1,2 and DP 1,3, respectively.

The reduced volume, for example, is used in the description of the temperature shift factor a_T of a pre-drawn sample, which is given by Brostow et al. [11]:

$$\ln a_T = 1/(a + c\lambda) + B/(\tilde{V} - 1) \qquad (15)$$

a, B and c are parameters, λ is the draw ratio. The reduced volume $\tilde{V}$ depends on T* via an EOS, while T* in turn depends on λ. Brostow[11] and also Hartmann[27] could show that the shift factor a_T obtained from p-V-T measurements is in good agreement with the results from other experimental methods. The reducing values can be determined from p-V-T measurements using an appropriate EOS, as for example the Hartmann equation,[30] Equation (12), which reduces to the Simha-Somcynsky equation at zero pressure. The definition of the reducing parameters may be different according to the EOS used. V, α, and κ are required to describe liquids in terms of Flory's theory of the liquid state.[7-9] Another still widely used approach to p-V-T equations of state is the relationship by van-der-Waals, and it has been shown by Roszkowski[31] that it can be obtained by simplification of Flory's equation of state. Other EOS were provided for example by Sanchez and Lacombe,[32] and Curro.[33] Simha's hole theory[34, 35, 36] extended to melts of compatible blends,[37] are able to describe experimental data over large spans of temperature and pressure. There are also some quite successful semi-empirical EOS, such as the Tait equation[38] for polymer melts, however, the Tait equation is not valid for semi-crystalline polymers.

$$V(p, T)/V(p = 0, T) = 1 - 0.0894 \ln [1 + p/B(T)] \qquad (16)$$

with

$$B(T) = B_0 \exp(-B_1 T) \qquad (17)$$

Bends in $V(T)_p$ graphs indicate phase transitions and the onset of molecular motions, the shift factor of relaxation processes and the activation energy can be calculated and give information about important structure-property relations.[39]

Surface tension γ of polymer melts is sometimes diff, there are relationships between other thermodynamic parameters and the surface tension or the interfacial free energy γ_{ii} between two condensed phases. Amóros et al. [40, 41] have studied the relationship between $\kappa(T)$ and the surface free energy. There are also theoretical approaches enabling the computation of γ from p-V-T data. These are based on Van-der-Waals' principle of corresponding states, which was extended by Prigogine et al. [42, 43, 44] to chain molecules. Patterson and Rastogi,[45] Siow and Patterson[46] and Dee and Sauer[47] developed equations to determine γ from p-V-T icult to determine experimentally. Some of the techniques are time consuming or require fairly elaborated equipment, e g, the 'imbedded fibre retraction method'.[48] However data respectively from the reducing *-parameters mentioned above using one of the appropriate EOS. Berry, Brostow and Hess[49] have successfully applied the theories on longitudinal polymer liquid crystals with varying mesogen concentration.

Breuer and Kosfeld[50] investigated the p-V-T properties of mixtures of polymers with solvents and gases. The behaviour of these systems is extremely important for their use as sealant and gasket or in the production of foams. They found that a linear relation between the compressibility and the pressure and the temperature, respectively, is only given when the system is in equilibrium. Sharp deviations were observed at the glass transition and when dissolved gas was liberated.

Starting from accurate compressibility measurements on atactic PS in the freezing region it was found by Rehage and coworkers[51, 52, 53, 54] that the relations for a second order transition are not applicable since the thermodynamic properties in the glassy state not only depend on temperature and pressure but also on the way of the glass formation, see also Hartmann and Haque.[27] This also applies to the limiting cases of very high pressures and temperatures (high pressure does NOT lead to a second order transition) and infinitely slow cooling at normal pressure (Gibbs-DiMarzio theory[55, 56] predicts a second order transition in this case). The path-dependence can be described by internal order parameters. Phase- and kinetic measurements have led to different conclusions about the multiplicity of linear independent order parameters. Later the same was found for polymer liquid crystals with the mesogenic groups on the side-chain [17] and as a constituent of the polymer backbone.[57, 58] Increasing pressure enlarges the range of existence of mesophases. Incorporation of rigid or mesogenic groups in the polymer chain does not change the character of the glass transition. The Ehrenfest[59] equations should not be valid at the glass transition that cannot be described as a second order transition.

While first order transitions obey the Clausius-Clapeyron equation:

$$\left(\frac{dp}{dT}\right)_{trans} = \frac{\Delta\tilde{S}}{\Delta T} = \frac{\Delta\tilde{H}}{\Delta\tilde{V}\cdot T} \qquad (18)$$

The Ehrenfest equations are:

$$\left(\frac{dp}{dT}\right)_{trans} = \frac{\Delta cp^*}{T\cdot\Delta\alpha^*} \qquad (19a)$$

$$\left(\frac{dp}{dT}\right)_{trans} = \frac{\Delta\alpha^*}{\Delta\kappa^*} \qquad (19b)$$

combining Equation (19a) and (19b) yields:

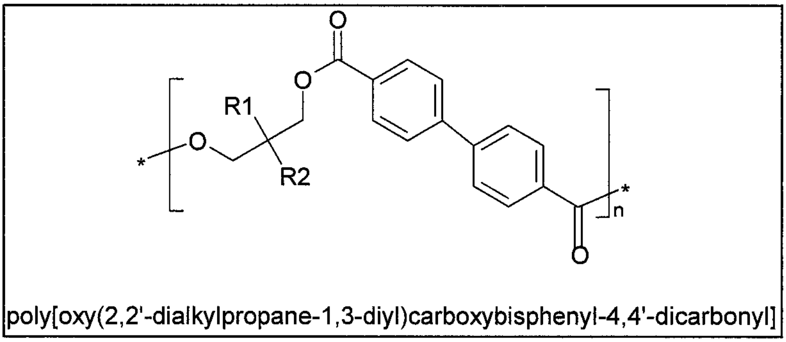
$$\frac{\Delta\alpha^*}{\Delta\kappa^*} = \frac{\Delta cp^*}{T\cdot\Delta\alpha^*} \qquad (20)$$

Rehage and Borchard[50] have shown that it is necessary to introduce parameters ξ describing the degree of internal order in a glass. If there is only one order parameter ξ necessary, either Equation (19a) **and** (19b) are valid or none of them. If only one of the Equations 19 is found to be valid at a glass transition this means that more than one parameter ξ has to be introduced. Meixner[60] and Davies and Jones[61] had already earlier predicted that:

$$\frac{\Delta c_p \cdot \Delta \kappa^*}{T \cdot \left(\Delta \alpha^*\right)^2} \geq 1 \qquad (21)$$

This was also verified for the polymers DP 1,1 to DP 1,3.[62] The pressure dependence of the glass transition temperature is usually found in the range from dT/dp = 0.2 K/MPa to dT/dp = 0.8 K/MPa. The pressure dependence of the glass transition temperature is not necessarily linear, see Figure 3. Increasing solidification pressure frequently leads to a densification of about 1% per 100 MPa. The pressure dependence of first order transitions are generally found to be around 0.2 K/MPa to 1 K/MPa.

Anormalous behaviour of melts can be analysed such as pressure induced melt-crystallization[63] or monotropic mesophase transitions.[54-56] Figure 7 and Figure 8 show an example. p-V-T measurements can also gain insight into the nature of certain phase transitions such as disordering processes hidden by melting processes as has been shown by Cantow and coworkers[64].



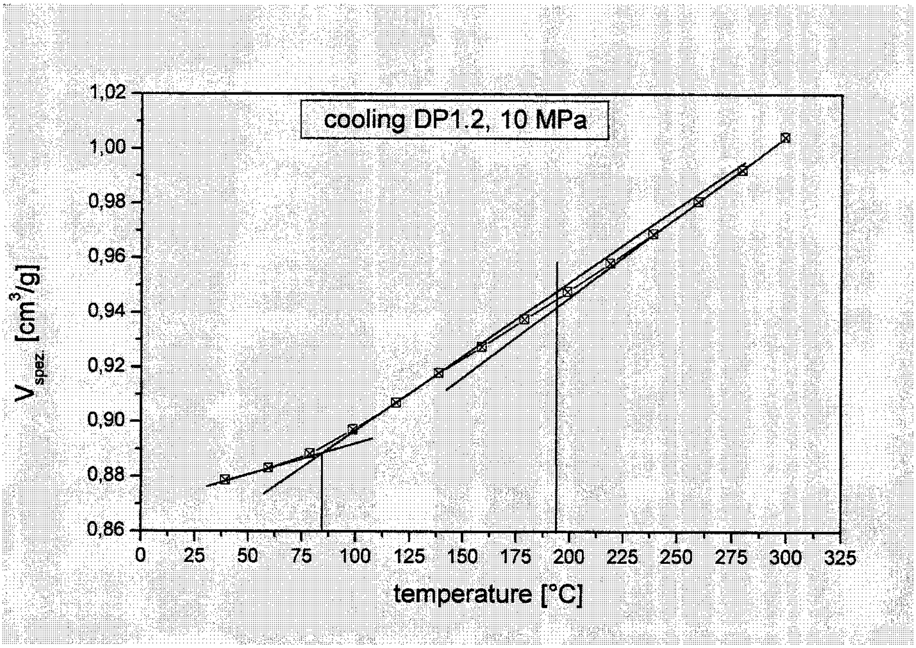


Figure 7. An example for an unusual phase transition: DP 1,2 shows an unusual increase of the specific volume with decreasing temperature, just as water at its melting point. The numbers indicate the number of carbons in the side chains

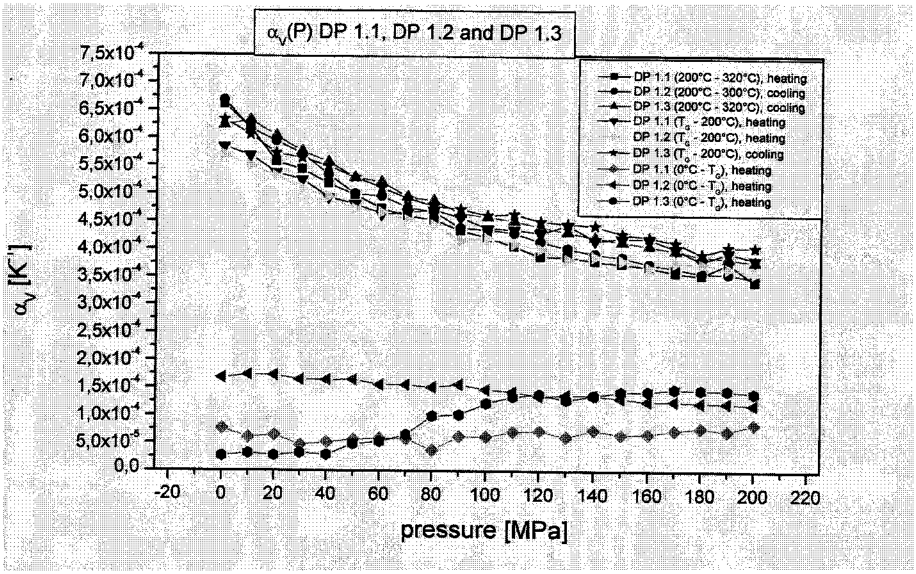


Figure 8. Unusual transition in the glassy state of the polymer DP 1,3 (-•-, bottom) compared with DP 1,1 and DP 1,3. The transition occurs in the pressure-dependence of the expansivity and is probably caused by packing effects of the growing side chain. The group of curves at the top describes the melt, the group of curves at the bottom describes a glass. In the case of DP 1,3 an increasing α with the pressure is observed. Rastogi[65] has recently described similar effects in poly(4-methyl-pentene-1).

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