

## **TRANSITIOMETRIC ANALYSIS OF PRESSURE EFFECTS ON VARIOUS PHASE TRANSITIONS**

*S. L. Randzio\**

Polish Academy of Sciences, Institute of Physical Chemistry, ul. Kasprzaka 44/52  
01-224 Warszawa, Poland

### **Abstract**

A scanning transitiometer has been used in investigations of 1st and 2nd order phase transformations in polymers. It was demonstrated taking as an example fusion of polyethylene at 200 MPa with a temperature scan as inducing variable that by recording simultaneously the rate of heat exchange and the rate of volume variations it is possible to determine in a single experiment the pressure derivative of temperature of this 1st order phase transition. For phase transformations similar to the 2nd order transitions the transitiometric analysis permits simultaneous measurements of pairs of thermodynamic derivatives which permit determination of pressure effects according to the Ehrenfest equations. For the glass transition in polystyrene at high pressures the pressure effect was similar independently of the pair of thermodynamic derivatives used (heat capacity and thermal expansivity or compressibility and thermal expansibility).

**Keywords:** glass transition, phase transition, polyethylene, polystyrene, pressure effects, transitiometry

### **Introduction**

When considering the pressure effect on a phase transition most people think of the Clapeyron equation

$$\frac{dT}{dp} = \frac{T\Delta V}{\Delta H} \quad (1)$$

where  $\Delta V$  and  $\Delta H$  are discontinuous changes of volume and enthalpy at the transition. This relation is valid only for so called (after Ehrenfest [1]) 1st order phase transitions. In such transitions there is no difference between the Gibbs energies in the two phases at equilibrium, but the derivatives of the Gibbs energy against temperature (entropy) and *vs.* pressure (volume) diverge at the transition. For 2nd order transitions both the Gibbs energy and its first derivatives are equal in the two phases, but the second order derivatives of the Gibbs energy (heat capacity, expansibility and compressibility) diverge at the transition. The following relations for the pressure effect on the 2nd order transition can be derived [1]:

\* Author for correspondence: fax: +48-39 12 02 38; e-mail: randzio@ichf.edu.pl

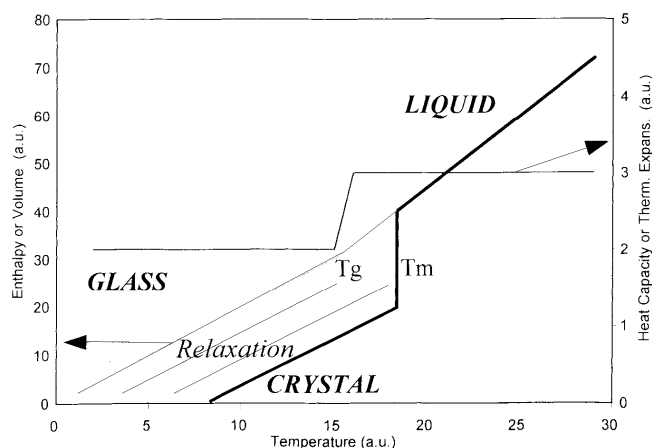
a) from the equality of the entropies in the two phases (' and ")

$$\frac{dT}{dp} = \frac{T \left[ \left( \frac{\partial V'}{\partial T} \right)_p - \left( \frac{\partial V''}{\partial T} \right)_p \right]}{(C_p)' - (C_p)''} \quad (2)$$

and b) from the equality of the volumes in the two phases (' and ")

$$\frac{dT}{dp} = \frac{\left( \frac{\partial V'}{\partial p} \right)_T - \left( \frac{\partial V''}{\partial p} \right)_T}{\left( \frac{\partial V'}{\partial T} \right)_p - \left( \frac{\partial V''}{\partial T} \right)_p} \quad (3)$$

Thus, when exploring pressure effects anyone must take into consideration the type of the transition. It is not so that the Clapeyron equation is valid for any phase transformation at equilibrium, as it is sometimes practised in studies of multiple phase transitions in food materials [2]. It is true that ideal 2nd order transitions occurring between two phases at equilibrium are very seldom. However, there are some common transformations which behave similarly to the ideal 2nd order transitions. Such a transformation is the glass transition. It occurs normally between a supercooled liquid and a glassy state. Both states are not equilibrium phases. A model representation of both 1st order transition (equilibrium crystallization and fusion) and glass transition is given in Fig. 1. At the temperature of the normal glass transition there is no abrupt changes of volume or enthalpy, there is only a change of the slopes of the enthalpy and volume curves. So, only step changes of the second order derivatives are observed at the glass transition temperature (shown in Fig. 1). However, the



**Fig. 1** An ideal behaviour of thermodynamic functions at the glass transition and at fusion-crystallization

glassy state can relax slowly into the direction of the crystal state and then recorded derivatives have more complicated character, because they also include effects related to the relaxation enthalpy or relaxation volume changes.

## Experimental

A description of the scanning transitiometric technique was given elsewhere ([3, 4] and references therein), thus, here will be presented only a short recalling limited to the pressure and temperature scanning. The experimental set-up consists of a high-pressure stainless steel calorimetric vessel placed in a calorimeter and connected to a high-pressure pump driven with a stepper motor controlled by a computer. By counting the number of motor steps and with the help of a proper calibration it is possible to record volume variations simultaneously with the calorimetric measurements. When the pressure scanning mode is used at constant temperature, the output variables recorded simultaneously correspond to variations of the thermal expansivity and compressibility as a function of pressure. With the isobaric temperature scan the recorded variables correspond to variations of the isobaric heat capacity and thermal expansivity.

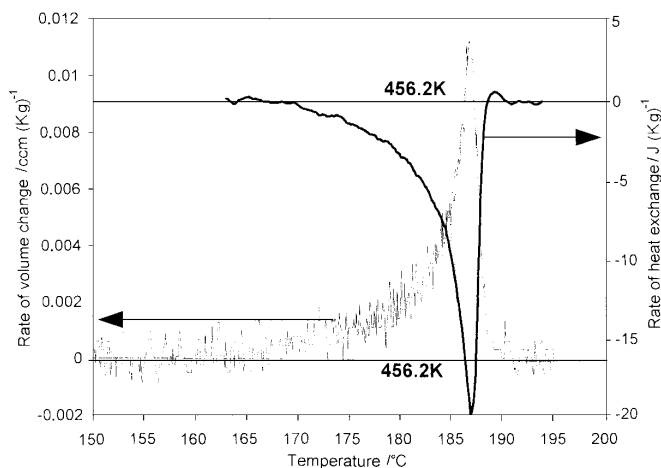
Medium density polyethylene (MDPE) used in the present study had the following characteristics:  $M_n=11460$ ,  $M_w=168500$ ,  $\rho=0.952 \text{ g cm}^{-3}$ , crystallinity=0.59.

Polystyrene (Approximate  $M_w$  250 000) was from Scientific Polymer Products, Cat. No. 039A in the form of pellets. Before use it was fused and solidified in a glass tubing I.D. 0.4 cm. After solidification the obtained polymer bar of 6 cm long was introduced into the calorimetric vessel. During measurements the two polymer samples were in direct contact with mercury.

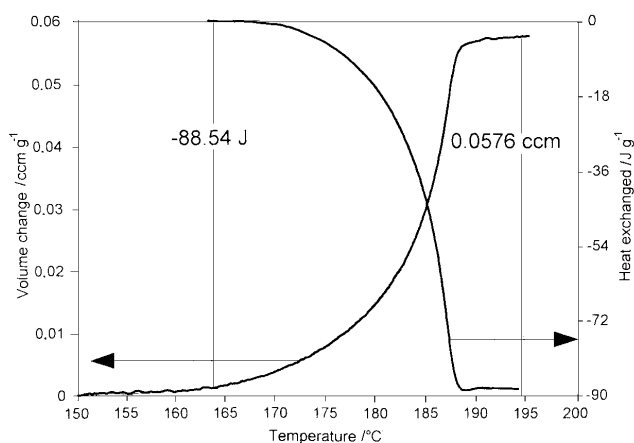
## Results

Results are presented in Fig. 2 of simultaneous measurements of the rate of volume variations and of the rate of heat exchanged in the course of fusion (correspond to the 2nd order derivatives of the thermodynamic potential change during the first order transition) of a MDPE induced by the isobaric temperature scan at a rate  $8.33 \cdot 10^4 \text{ K s}^{-1}$  at 200 MPa. The temperature of the transition was determined from the intercept of the slope of the main fusion process with the base line. It is worth noting that the rates of variations with temperature of both volume and heat gave the same value of the temperature of fusion. Variations of volume and of enthalpy in the same process obtained by integration of curves from Fig. 2 are presented in Fig. 3. By introducing obtained values into the Clapeyron equation the pressure derivative of the temperature of the transition is obtained at 200 MPa in a single experiment. The obtained value ( $0.297 \text{ K MPa}^{-1}$ ) is in a fairly good agreement with the literature values [5].

The investigation of transformations similar to the 2nd order transitions is much more difficult, because the measured effects are much less pronounced. Results of simultaneous recording of heat and volume variations at the glass transition in polystyrene induced by isobaric temperature scan at a rate  $2.75 \cdot 10^{-3} \text{ K s}^{-1}$  at pressure



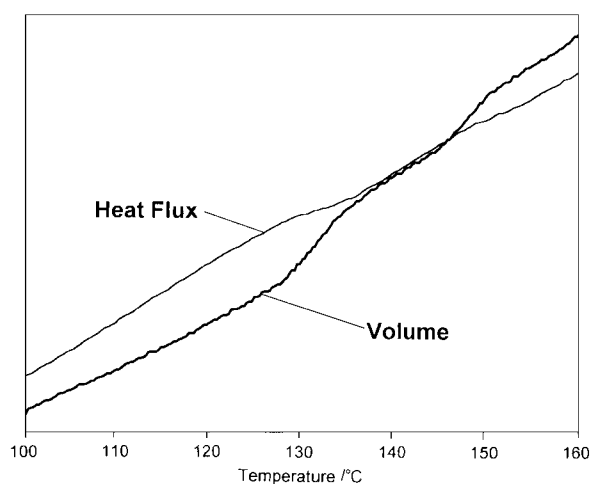
**Fig. 2** A transitiometric analysis of fusion of a medium density polyethylene (MDPE) induced by an isobaric temperature scan at a rate  $8.33 \cdot 10^{-4} \text{ K s}^{-1}$  at 200 MPa;  $T(\text{C}) = T(\text{K}) - 273.15$



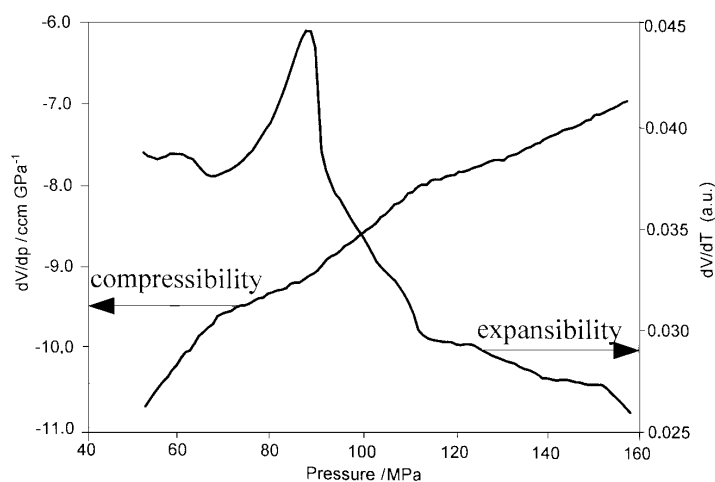
**Fig. 3** Volume and enthalpy variations at fusion of a medium density polyethylene (MDPE) induced by an isobaric temperature scan at a rate  $8.33 \cdot 10^{-4} \text{ K s}^{-1}$  at 200 MPa;  $T(\text{C}) = T(\text{K}) - 273.15$

100.3 MPa are presented in Fig. 4. One can see from both volume and heat flux variations that the glass transition under these conditions is a rather complex process. This complex nature of the glass transition in polystyrene is also observed in isothermal pressure scanning measurements. Results of investigation of the glass transition in polystyrene induced by isothermal decompression at a rate  $0.01 \text{ MPa s}^{-1}$  at 403 K are presented in Fig. 5. Here, the simultaneous variations of the compressibility and of the thermal expansivity (2nd order derivatives of the thermodynamic potential) are given. The pressure derivative of the temperature of the glass transition determined

from both isobaric and isothermal measurements is equal to about  $0.31 \text{ K MPa}^{-1}$ . This result is interesting, especially with respect to the simultaneous measurements of compressibility and thermal expansivity variations at the glass transition, because it is usually accepted that the variations of these thermodynamic derivatives at the glass transitions are caused by changes in different molecular motions [6, 7]. A more detailed discussion of the observed complexity of the glass transition in polystyrene under high pressure will require more experiments, possibly with polystyrene samples with various chain lengths. It is known that even at normal pressure the polydispersity of the polystyrene chains greatly influences the glass transition temperature [8].



**Fig. 4** Volume and heat flux variations at the glass transition of polystyrene induced by an isobaric temperature scan at a rate  $2.75 \cdot 10^{-3} \text{ K s}^{-1}$  at  $100.3 \text{ MPa}$ ;  $T(\text{C})=T(\text{K}) - 273.15$



**Fig. 5** A transitiometric analysis of the glass transition in polystyrene induced by an isothermal pressure scan at a rate  $0.01 \text{ MPa s}^{-1}$  at  $403 \text{ K}$

## Conclusions

The use of transitiometric analysis with temperature and pressure as inducing variables permits to record simultaneously pairs of 2nd (or 1st) order derivatives of the thermodynamic potential, such as thermal expansivity and compressibility (or entropy/heat and volume changes) and isobaric heat capacity and thermal expansibility (or enthalpy and volume changes). Those derivatives are the most important parameters in determination of the pressure effects on the phase transformations and are very helpful in analysing the type of the transition under investigation. The simultaneous determination in a single experiment of pairs of thermodynamic derivatives as a function of the inducing variable, temperature or pressure, allows to get a thermodynamic description of substances and materials with an easy experimental set-up. The instrument is extremely useful, especially for investigations of transformations between phases being not in the equilibrium state or being unstable for other reasons, where reproducibility of the initial state of the samples under investigation can be very poor.

## References

- 1 P. Ehrenfest, Proc.Kon.Akad.Wetench., 36 (1933) 153.
- 2 A. H. Muhr, R. E. Wetton and J. M. V. Blanshard, Carbohydrate Polymers, 2 (1982) 91.
- 3 S. L. Randzio, Chem. Soc. Rev., 25 (1996) 383.
- 4 S. L. Randzio, J. Thermal Anal., 48 (1997) 573.
- 5 T. Davidson and B. Wunderlich, J. Polym. Sci. A2:Polym. Phys., 7 (1969) 377.
- 6 W. Kauzmann, Chem. Rev., 43 (1948) 219.
- 7 I. Havlíček, M. Ilavsky and J. Hrouz, J. Macromol. Sci.-Phys., B21 (1982) 425.
- 8 A. A. Mansour and B. Stoll, Colloid Polym. Sci., 271 (1993) 834.