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ISOTHERMAL AND ISOBARIC PVT-MEASUREMENTS OF ATACTIC POLYMERS

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Abstract

It is evidenced that due to the kinetic character of the glass transition as a 'freeze in' process, PVT measurements extended over the glass transition range depend not only on the thermal history but also on the pressure acting during the formation of the polymeric glasses. As a consequence metastable glasses are formed which show during heating of the glassy polymer through the glass transition range 'volume relaxation zones', characterized by a retarded increase or even decrease of the volume. The width of the 'relaxation zone' increases with increasing pressure and depends additional on the mode of operation used during the PVT measurements. In the same time a pressure induced shift of the glass temperature to higher temperatures is observed, the shift being the greater the stiffer the polymer, i.e. the higher the glass temperature of the polymer at atmospheric pressure. Due to the metastable character of polymeric glasses the evaluation of universal equations of states is thus not ingenious for polymeric glasses, because the deduced EOS will be valid only for that given glass characterized by a well defined thermal and pressure history. Additionally the EOS is influenced by the unknown time dependent aging and relaxation processes within polymeric glasses.

Keywords: polymeric glasses, polymers, PVT measurements

Introduction

The description of any thermodynamic closed system requires the knowledge of the equation of state, which enables the evaluation of the corresponding Helmholtz (free) energy of the system and all other related thermodynamic functions. Thus knowing the equation of state the thermodynamic equilibrium of the system is unequivocal defined. For real systems, however, instead of the

state parameters, pressure (p), volume (v) and temperature (T), the reduced variables, $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ are used for defining an universal equation of state

$$f(\tilde{p}, \tilde{v}, \tilde{T}) = 0$$

The reduced variables are evaluated using the so called 'reduction parameters'. The characteristics of any thermodynamic system are thus related with these 'reduction parameters', which are accessible via expansion and compressibility coefficients obtained from PVT-data. The respective expressions of the 'reduction parameters' are specific of the different equation of state theories [1]. Alternatively, the reduction parameters can be evaluated by fitting the PVT-data of the corresponding system.

Thus the knowledge of PVT-data is essential for the thermodynamic characterization of polymers. The form of the respective equation of state and of the related functions (solubility parameters, for instance) depends, however, on the preferred equation of state theory [2]. It has been shown, that the EOS are unequivocal only for polymers in the molten state and solution and universal 'mastercurves' for the pressure dependence of the volume are feasible [3].

For atactic polymers, however, an additional problem arises which is related to the kinetic character of the glass transition as a freeze-in process (Fig. 1). Accordingly the thermodynamic characterization of polymeric glasses supposes the knowledge of a supplementary kinetic dependent 'ordering parameter' [4].
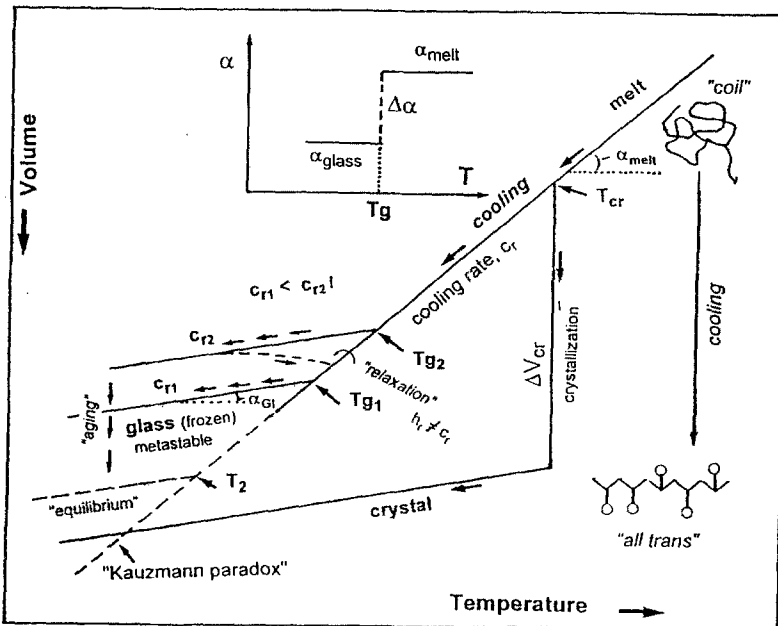

Fig. 1

Due to the kinetic character of the glass transition, polymer glasses show time dependent aging and relaxation phenomena. The relaxation is noticeable in PVT-diagrams during heating through the glass transition range by a given zone of less increasing or even decreasing volume. Quach and Simha [5] have related this 'volume' relaxation to the transition back to the glassy state of the pressurized polymer melt. Zoller and Hoehn [6] have shown that the relaxation zone is enlarged by increasing the pressure.

In Fig. 1 is presented schematically the temperature dependence of the polymeric volume at isobaric conditions. Coiled polymer particles present in the melt may crystallize during cooling, with the condition that they have configurational ordered structures (i.e. show iso- or syndio-tacticity). The crystal-lization is characterized by a discontinuity of the volume at a well defined crystallization temperature (the 'crystallization' volume, ΔV_{cr}). According to Ehrenfest, crystallization is thus a thermodynamic first order transition (the discontinuity is shown by the volume, which is a first order derivative of the Gibbs free energy, $V = (\delta G/\delta P)_T$). Crystallization may be prevented, however, if the cooling rate exceeds the crystallization rate.

Configurational non ordered, atactic polymers show during cooling a tranzition too, evidenced by a discontinuity, $\Delta \alpha$, of the expansion coefficient, $\alpha = V^{-1}(\delta^2 G/\delta P \delta T)$. This is generally characteristic of a thermodynamic second order transition (see insertion in Fig. 1).

Nevertheless, the simultaneous dependence on the cooling rate supports the kinetic character of the glass transition of polymers, which in fact is a 'freeze in' process. Polymer glasses are thus thermodynamically metastable, characterized additional by an ordering parameter [4]. The existence of a real thermodynamic second order transition in atactic polymers is, however, supported by the observation that by extrapolation to low temperatures, the specific volume of the random coil becomes smaller than the volume of the ordered crystall, which from the thermodynamic point of view is a nonsense ('Kauzmann paradox'). The theoretical predicted existence of an 'equilibrium glass' explains the experimentally observed aging and relaxation phenomena shown by the real polymeric 'frozen in' glasses.

Taking into account that the glass transition of polymers as a 'freeze in' process depends on operating parameters, i.e. cooling resp. heating rates, the question arises if and how this process is influenced by pressure. Consequently in the following results of PVT-studies will be presented concerning the influence of pressure on the glass transition of both polystyrenes of different molecular weights and atactic polymers of different stiffnesses (i.e. polymers with different glass temperatures, T_g).

Experimental

The characteristics and provenience of the polymers used in the PVT studies are shown in Table 1.

Table 1 Characteristics of polymers used for PVT-measurements

Polymer	M_w	M_w/M_n	Symbol
Polystyrene[a]	2 300	1.09	PS 2
	5 000	1.19	PS 5
	43 300	1.03	PS 43
	54 000	1.05	PS 55
	1 200 000	1.06	PS 1.2 Mio
Poly(2,5-dimethyl phenylene oxide)[a]	13 100	2.73	PPO
Poly(cyclohexyl-methacrylate)[b]	62 000	1.44	PCHMA
Poly(methylmethacrylate)[c]	108 000	1.08	PMMA
Polyvinylchlorid[d]	37 400	2.23	PVC

[a] samples of BASF, -PS by anionic polymerization; [b] obtained by anionic polymerization in our laboratory; [c] sample of Rhöm by group transfer polymerization; [d] sample of Aldrich.

The PVT measurements were performed using the GNOMIX PVT apparatus of Zoller [7] applying both the isothermal and isobaric mode of operation. In the isothermal mode the data were aquired along isotherms, both for increasing and decreasing pressure. The respective glasses were all obtained by cooling of the polymer melt at 10 MPa. In the isothermal mode with increasing pressure, the starting pressure was of 10 MPa, the pressure being then increased in steps of 40 MPa up to 200 MPa. Subsequently the temperature has been increased, the glass depressurized to 10 MPa and the isothermal measurement cyclus has been repeated at the new temperature. In the isothermal mode with decreasing pressure, the sample has been first pressurized to 200 MPa. Subsequently the pressure was decreased in steps of 40 MPa. The data for atmospheric pressure (0 MPa) have been estimated by extrapolation. In the isobaric modes of operation the polymeric glasses were obtained from the melt, either at 10 MPa or at the pressure used in the subsequent step of isobaric measurement. Both cooling and heating rates were of 4 K min^{-1}.

Results and discussion

Influence of the mode of operation and molecular weight on the pressure dependent T_g-shift

Typical PVT-diagrams are illustrated in Fig. 2 for PS ($M_W=1.2\times10^6$). It is evident that the shape of the PVT curves and mainly the width of the 'relaxation zone' depend on the mode of operation. Except the case where the polymeric
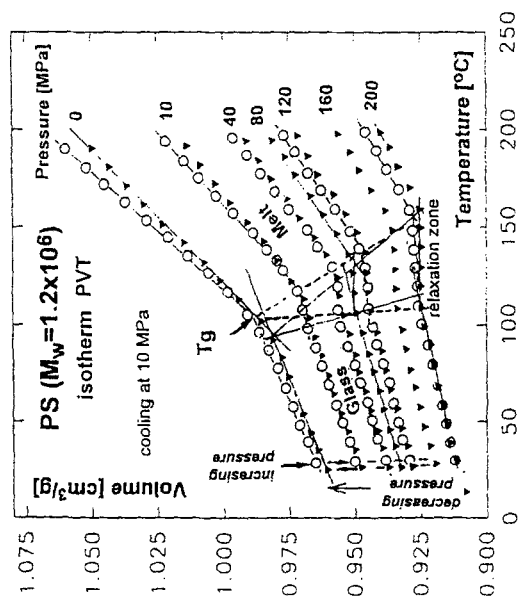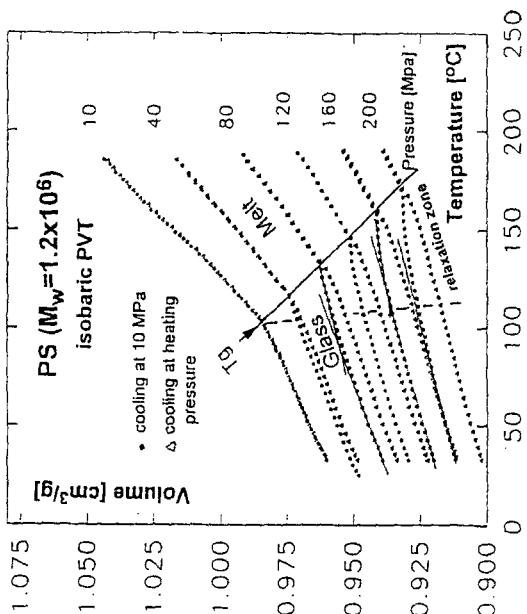
Fig. 2

glasses were obtained at those pressures which then were used for the sub-
sequent isobaric measurements at a constant heating rate, relaxation zones are
observed in the glass transition range, which broaden with increasing pressure
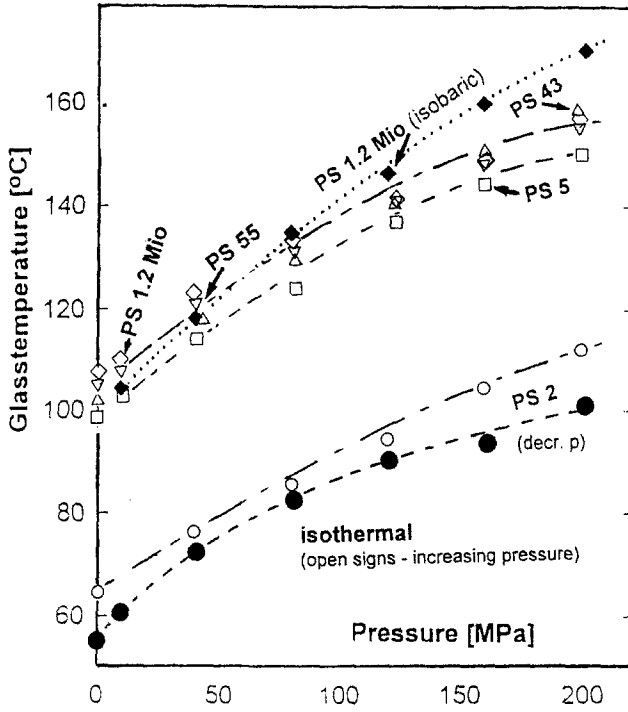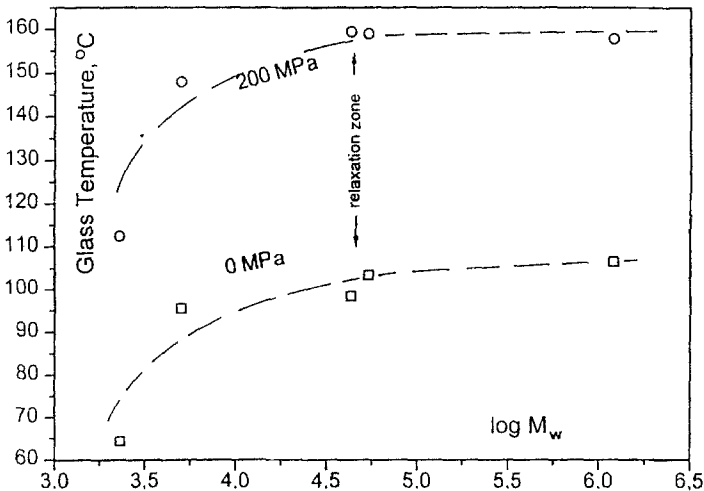

Fig. 3

Fig. 4

[8]. The width of the relaxation zones depends evidently on the mode of operation. Simultaneously a shift to higher temperatures of the glass temperature is observed (defined by the transition into the polymeric molten state, characterized by the higher expansion coefficient, α_{melt}, indicated by arrows in Fig. 2).

The pressure dependence of the glass transition temperature of the different PS is illustrated in Fig. 3. For clarity are presented data obtained in the isothermal mode with increasing pressure. To evidence the influence of the mode of operation additionally are presented T_g data, obtained either using the isothermal mode with decreasing pressure (exemplified for PS 2) or the isobaric mode of operation (exemplified for PS 1.2 Mio).

The molecular weight dependence of the T_g-shift to higher temperatures with increasing pressure is illustrated in Fig. 4. Comparatively the T_g data obtained in the isothermal mode with increasing pressure for atmospheric pressure (0 MPa) and 200 MPa, respectively is presented. The temperature shift is in the same time related to the width of the relaxation zones observed in the PVT diagrams [8].
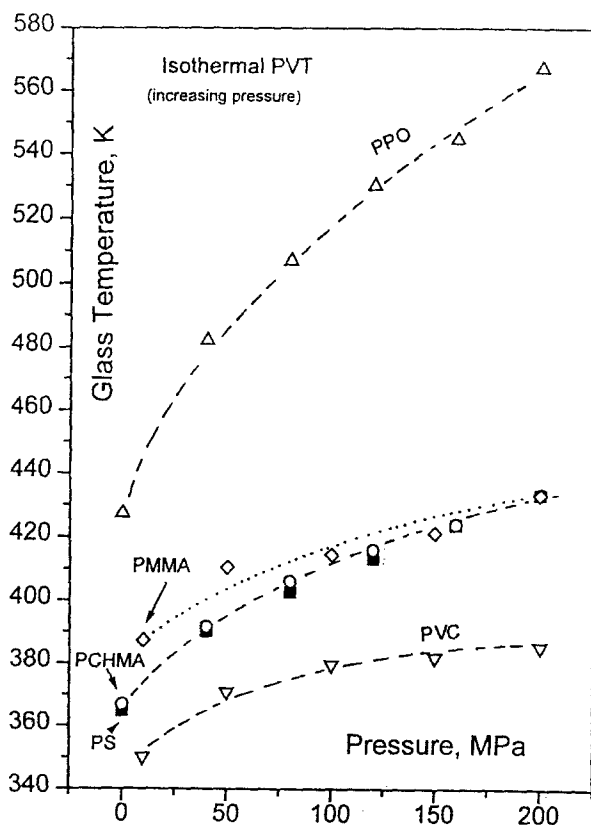

Fig. 5

Dependence of the pressure induced T_g-shift on the nature of the polymer

The pressure dependence of the glass temperatures of the studied amorphous polymers is illustrated in Fig. 5, using data obtained in the isothermal mode with stepwise increasing pressure during the measurements. It is remarkable that the shift of the T_g to higher temperatures is generally as larger as higher the glass temperature at atmospherhic pressure of the respective polymer, i.e. as stiffer the amorphous polymer is.
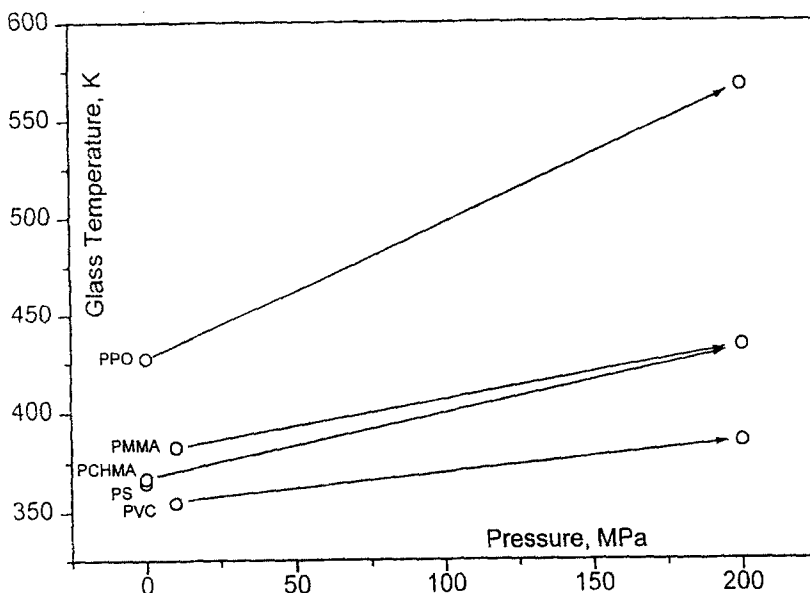

Fig. 6

The larger shift to higher temperatures of the glass temperatures of amorphous polymers is in the same time accompanied by a corresponding increase of the width of the volume relaxation zone [9]. The steeper increase of the glass temperature of the stiffer polymers is supported by the respective slopes of the straight lines connecting the glass temperatures of the polymers for atmospheric pressure and 200 MPa (Fig. 6) as well as by the observed almost linear correlation between the respective glass temperatures (Fig. 7) A possible explanation assumes that the 'free volume' fraction responsible for the release of mobilities characteristic of the glass transition has to be as larger as stiffer the polymer. As a consequence the pressure influence, i.e. the effect of comprimation on the overall volume will be also larger. To reach thus anew at the increased pressure the respective 'free volume' fraction responsible for the glass transition a stronger expansion is needed.

In conclusion due to the kinetic character of the glass transition, polymeric glasses of different thermodynamic metastable structures are obtained, depend-
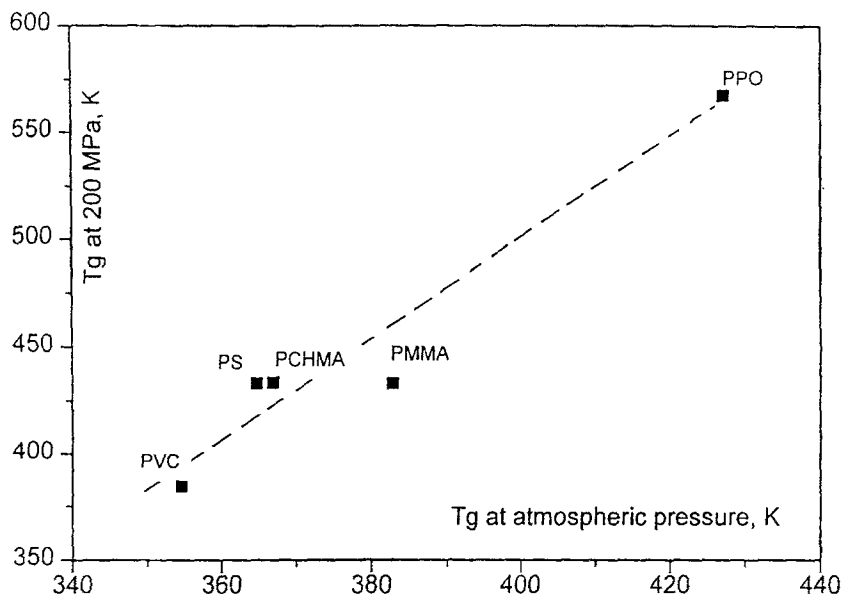
Fig. 7

ing not only on the thermal history (cooling and heating rates), but also on the pressure applied during the glass formation. The metastability of the glasses is confirmed by the 'relaxation zones' observed in PVT measurements. Accordingly any attempt of formulation of an equation of state for polymeric glasses will fail because the estimated characteristic EOS-parameters are dependent on the history of glass formation and additionally are related to the time dependent 'aging and relaxation' of polymeric glasses. Both the pressure dependent shift of T_g to higher temperatures and the increase of the width of the 'relaxation zone' are generally the more significant the stiffer the polymer.

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