P–V–T measurements of polystyrene materials [1]

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Abstract

Pressure, temperature and specific volume measurements of industrial polystyrene materials (a standard amorphous and atactic polystyrene, a modified polystyrene and a rubber polystyrene modified with carbon black) have been studied by barodilatometric analysis, thermobarometric analysis and differential scanning calorimetry. The isothermal compressibility, isobaric expansion and isochoric pressure coefficients of both glassy and visco-elastic phases were deduced from experiments. The isothermal compressibility in the visco-elastic phase is the only coefficient that cannot be considered to be independent of pressure and temperature, because it involves a volume dependence for the heat capacity at constant volume. Simple equations of state are proposed for both phases. The boundary curves between the phases were determined: they are straight lines in the pressure and temperature ranges studied. Their slopes were compared with the data given by Ehrenfest's relation. The influence of the composition on the specific volume, isobaric expansion and isothermal compressibility coefficients is discussed.

INTRODUCTION

For most industrial working-up operations on polymers (injection, extrusion, moulding, compression), the temperature and pressure conditions have a great influence on the resulting products. Both for process control on the one hand and for the prediction of materials behaviour on the other hand thermodynamic data should be determined under conditions which are similar to the real process conditions. In general, differential thermal analysis and scanning calorimetry are both convenient for predicting the

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thermal behaviour of polymers under the customary conditions of use but are not sufficient for predicting behaviour during working-up operations, when the polymers are often submitted to both high pressure and temperature.

Using two complementary analytical techniques, we have investigated the $P-V-T$ relationship (P, pressure; V, specific volume; T, temperature) for three industrial polymers (polystyrenes), in order to characterize these materials by their phase diagrams and equations of state and to allow the comparison of their thermodynamic properties.

EXPERIMENTAL

Materials

The materials studied were three thermoplastic polymers supplied by Atochem: a standard amorphous and atactic polystyrene (here called PSK); a rubber polystyrene modified with a polybutadiene as the dispersed phase (here called PSCH); and a rubber polystyrene modified with carbon black (here called PSN). These materials were supplied as granules.

Instrumentation

Isothermal pressure–volume measurements using barodilatometric analysis (BDA) were performed with PVT 100 apparatus (Rapra Technology Ltd.). The measuring technique involves increasing the pressure from atmospheric pressure while maintaining a constant temperature. The equipment contains a stainless steel bellows with mercury as the containing fluid: any volume change is converted by the bellows into a linear movement which is measured by a displacement transducer. The bellows are surrounded with oil and enclosed within a pressure vessel. The pressure and temperature ranges were respectively 0–200 MPa and 300–500 K. Thus this technique yields pressure–volume diagrams and interpolated temperature–volume diagrams.

Isochoric pressure–temperature measurements using thermobarometric analysis (TBA) [1] were carried out with a Metabolemeter [2] (MAB 02, MTM Leader Ltd.), in which the pressure values of a sample enclosed in a rigid steel cell are recorded versus temperature. Any volume change is converted into a pressure change which is directly detected by means of a pressure transducer used as the bottom of the cell. The pressure and temperature ranges were respectively 0–120 MPa and 300–480 K. This measuring technique yields pressure–temperature diagrams (thermobarograms) and the associated $P-T$ phase diagrams [3]: measurements were made in a continuous mode, thus yielding the $P-T$ data in one phase with a better accuracy than the interpolated data obtained by BDA.

Complementary calorimetry measurements were performed using a differential scanning calorimeter [1], (FP 85, Mettler) in order to obtain the glass transition temperature (T_G^0) under atmospheric pressure.

Experimental procedures

For BDA studies, the material was introduced into the apparatus in granular form. To reach the proper conditions, after each isothermal measurement, the pressure on the sample was released down to atmospheric pressure at a constant temperature; the temperature of the sample was then raised to a higher value under atmospheric pressure.

For TBA measurements, granules of material were cut into small pieces, then put into the cell and melted up to about 430 K while under atmospheric pressure; the sample was kept at high temperature for a few minutes to release included gas. Then the cell was cooled down to room temperature and finally sealed. Measurements can be performed during heating and cooling at the maximum rate of 4 K min^{-1}. The isochoric thermobarogram systems were obtained from modifications of the initial filling conditions [3].

For fresh samples, TA thermograms were plotted, corresponding to a heating rate of 4 K min^{-1}.

In the solid state, measurements carried out with these procedures are dependent on the history of the sample.

RESULTS

Figures 1 and 2 show respectively the BDA curves $V = f_T(P)$ and interpolated curves $V = f_P(T)$ for the three samples. The P–V curves show a continuous change between the glassy phase and the visco-elastic phase with the slope given by

$$\left(\frac{dV}{dP} \right)_P = \chi V$$

where χ is the isothermal compressibility coefficient; the T–V curves exhibit an anomaly in the slope given by

$$\left(\frac{dV}{dT} \right)_P = \alpha V$$

where α is the isobaric expansion coefficient relative to the glass transition under various pressures. Both the χ and α coefficients, in the glassy phase and in the visco-elastic phase, are practically independent of the temperature and only slightly dependent on the pressure; in practice these coefficients can be considered as constant, within 5% maximal error.
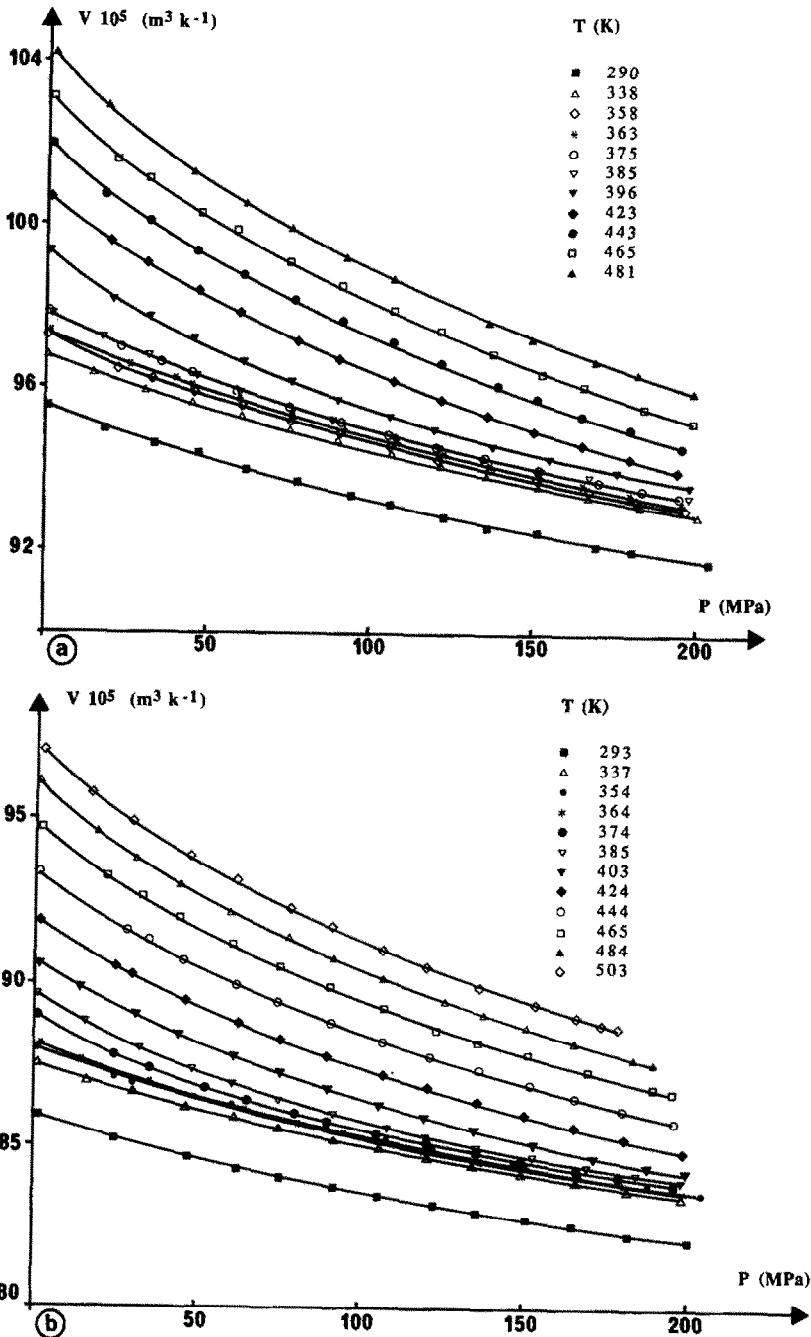
Fig. 1. Isothermal pressure–volume curves for polystyrene materials: (a) PSK; (b) PSCH; (c) PSN.
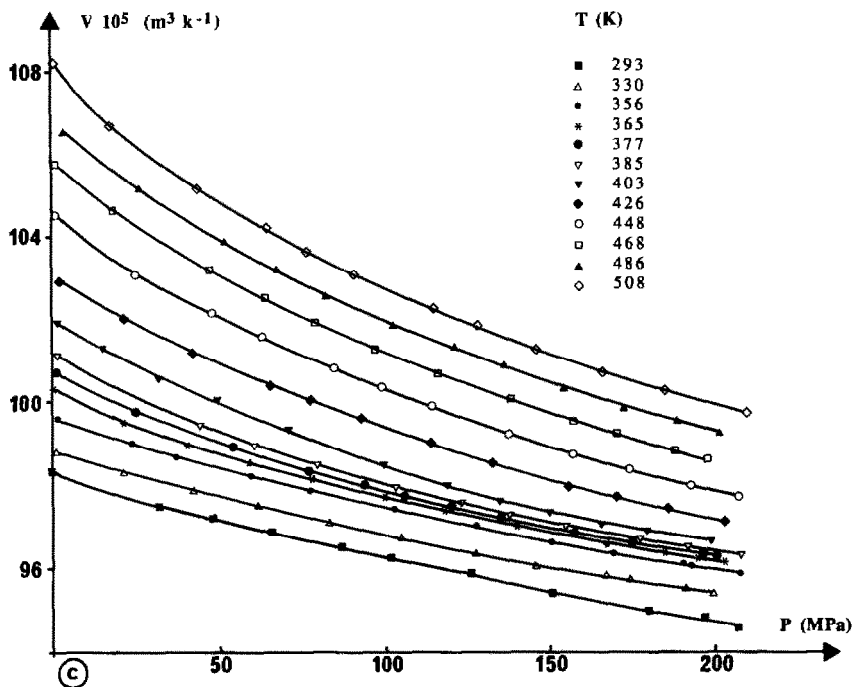
Fig. 1. (continued).

Examples of thermobarograms are given in Fig. 3. All the P–T curves show a clear progressive change in the slope given by

$$\left(\frac{dP}{dT}\right)_V = \frac{\alpha}{\chi} = \beta P$$

where β is the pressure coefficient, corresponding to the glass transformation under pressure [4,5]. For each polystyrene material studied, the P–T curves can be superposed by translations. The slope can be considered as constant (within 3% maximal error) in the glassy phase but decreases progressively in the visco-elastic phase, at both high pressure and temperature; these types of behaviour are qualitatively and quantitatively reproducible for several different samples of each compound as well as for two successive cycles on the same sample. For the heating and cooling rates available with the apparatus, no significant difference was observed on the thermobarograms. Figure 3(b), obtained for two heating (curves 1 and 3) and cooling (curves 2 and 4) cycles on PSK, shows the existence of a hysteresis phenomenon, linked to the initial relaxation of the material. This hysteresis remains (curves 3 and 4) as long as the sample has not relaxed. The time required to obtain the complete relaxation of the sample is about 12 h; the thermobarograms obtained after complete relaxation are then perfectly superimposable.
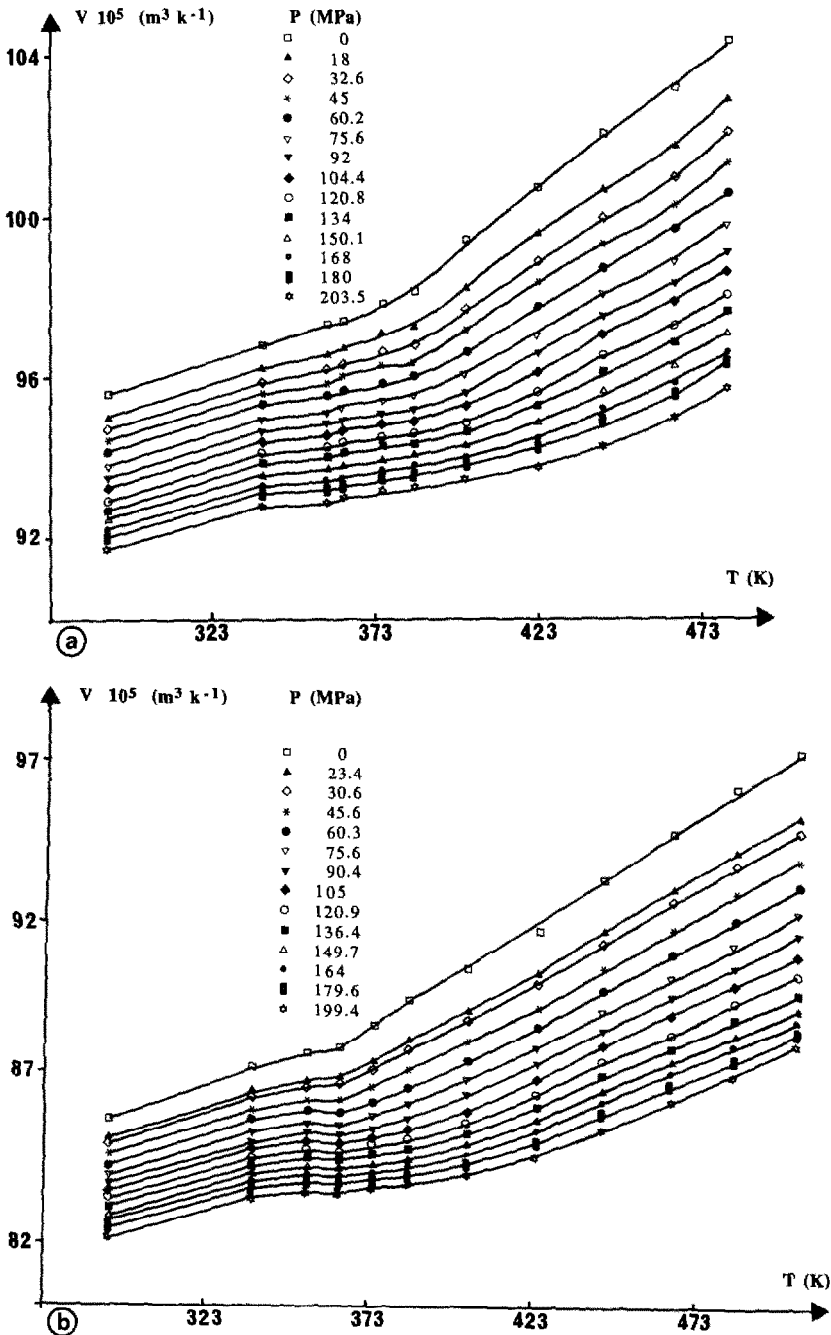
Fig. 2. Interpolated isobaric temperature–volume curves for polystyrene materials: (a) PSK; (b) PSCH; (c) PSN.

V 10⁵ (m³ k⁻¹) P (MPa)

□	0
▲	6
◇	32.1
*	48
●	66
▽	87.2
▼	102
◆	126.2
○	150.8
■	180
△	197
●	207

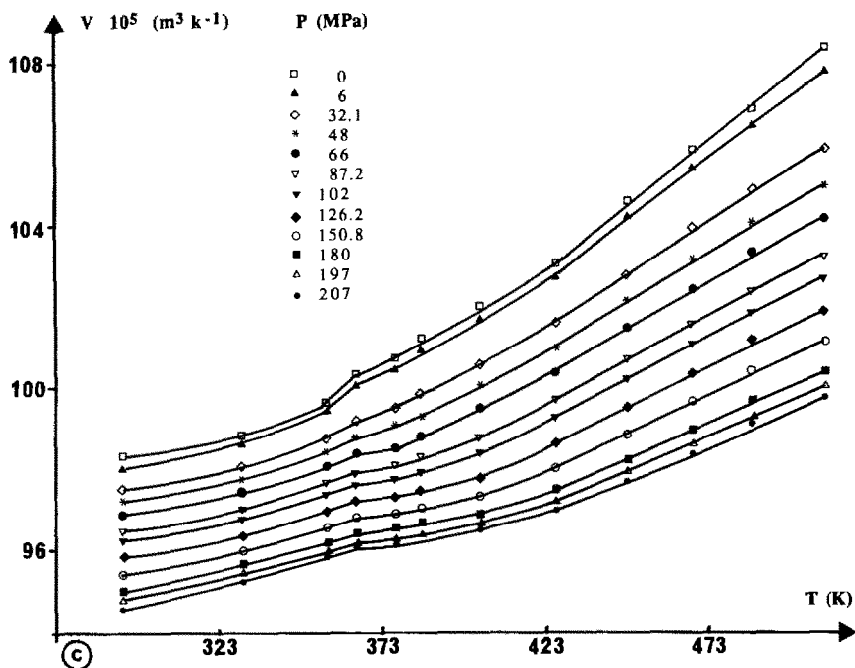108

104

100

96

T (K)

323   373   423   473

Ⓒ

Fig. 2. (continued).

TABLE 1

Thermodynamic data for the PSK, PSCH and PSN polystyrene materials for both glass phase (GP) and visco-elastic phase (VeP)

	PSK		PSCH		PSN	
	GP	VeP	GP	VeP	GP	VeP
T_G^0 (K) for P atm. [a]	376		363		368	
$(dP/dT)_{exp}^E \times 10$ (MPa K^{-1}) [b]	29.4		29		28.7	
$(dP/dT)_{cal}^E \times 10$ (MPa K^{-1}) [b]	20		16		9	
$(\alpha/\chi)_{exp} \times 10$ (MPa K^{-1}) [c]	6.5	9 [f]	6.5	8.5 [f]	6	9 [f]
$\alpha_{exp} \times 10^4$ (K^{-1}) [d]	2.5	5.7	3.5	6	2	4.7
$\chi_{cal} \times 10^4$ (MPa^{-1}) [d]	3.8	6.3 [f]	5.3	7 [f]	3.3	5.2
$A \times 10^6$ (MPa^{-1}) [e]		−4.2		−6		−2.6
$B \times 10^{10}$ (MPa^{-1}) [e]		1.5		1.1		1.8

[a] T_G^0, glass transition temperature under atmospheric pressure.

[b] $(dP/dT)_{exp}^E$ and $(dP/dT)_{cal}^E$, experimental and calculated slopes of the boundary line.

[c] $(\alpha/\chi)_{exp}$, experimental slope of the thermobarograms.

[d] α_{exp} and χ_{cal}, experiment isobaric expansion and calculated isothermal compressibility coefficients.

[e] A and B, coefficients in the equation of state for the visco-elastic phase.
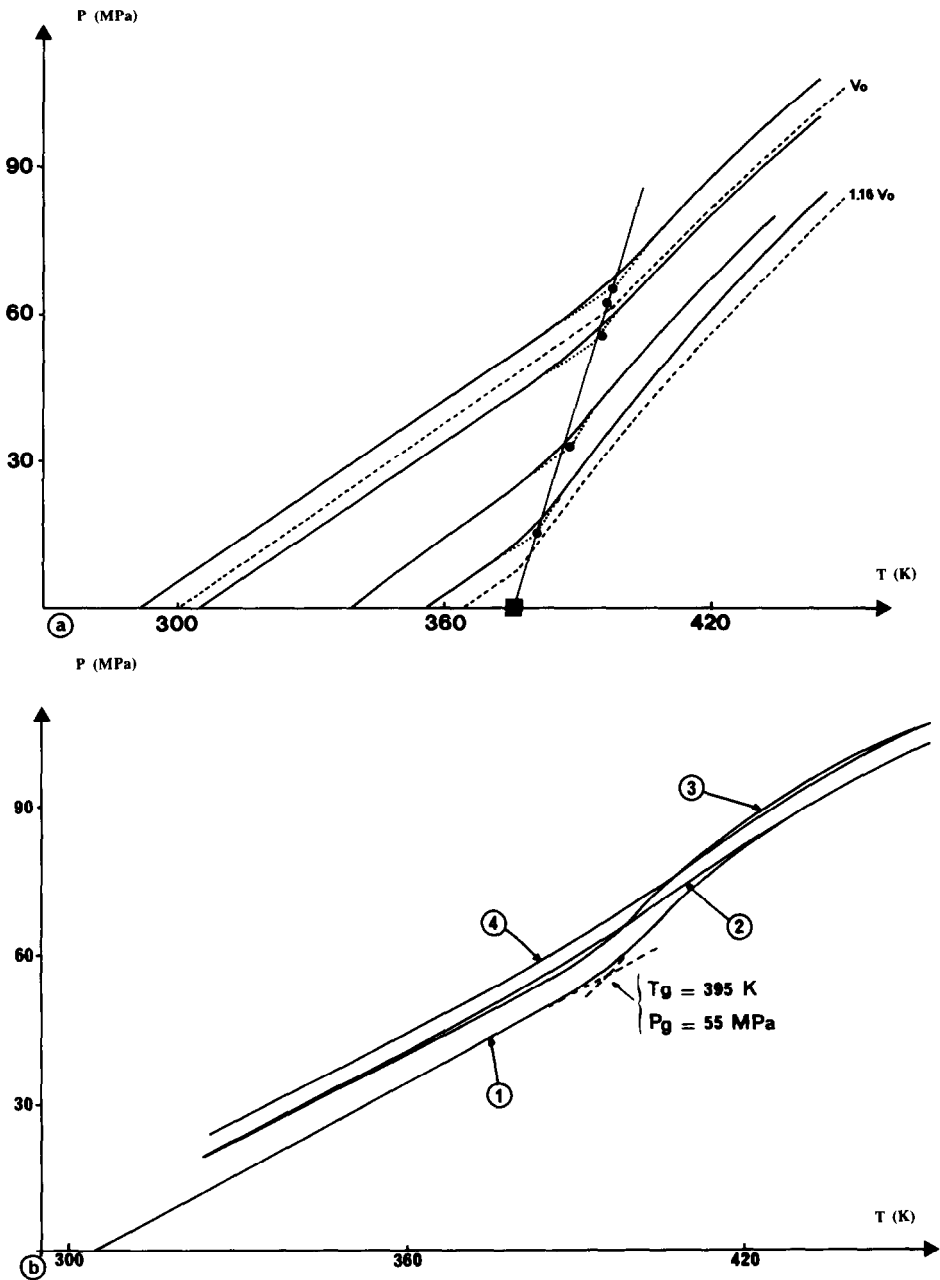
[f] Just after T_G.

Fig. 3. Isochoric thermobarograms for polystyrene materials (●, experimental glass transition temperature for thermobarograms; ■, experimental glass transition temperature for thermograms; ———, experimental thermobarograms; – – –, calculated thermobarograms): (a) PSK; (b) cycles for PSK (curves 1 and 3, on heating; curves 2 and 4, on cooling); (c) PSCH; (d) PSN.
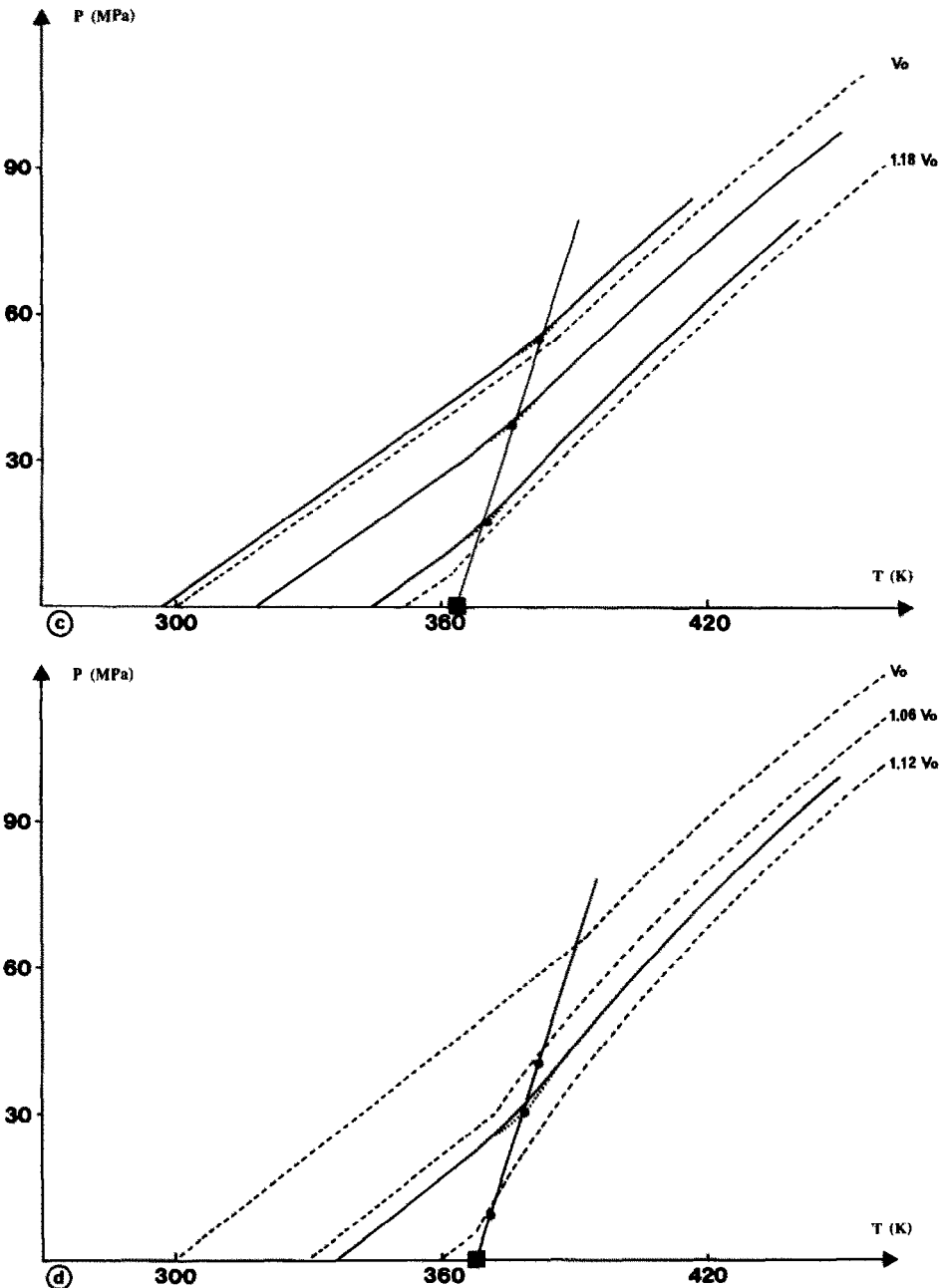
Fig. 3. (continued).

For the three compounds, the mean values for χ, α and $P\beta$ in the glass phase, for α in the visco-elastic phase, and data for χ and $P\beta$ near the glass transition in the visco-elastic phase, were determined from Figs. 1–3

and are reported in Table 1. Because the glass transition cannot be detected on the $P-V$ curves, the χ coefficient in the visco-elastic phase near the transformation is calculated from the α and $P\beta$ data (see Table 1). The pressure and temperature operating ranges of the apparatus were such that the melting point was not reached. The glass transition temperatures under atmospheric pressure T_G^0 obtained from the thermograms are reported in Table 1.

DISCUSSION

Equation of state

In the glassy phase, the $P-V-T$ equation of state that fits with experimental data is given by the relation

$$V_G = V_G^0[1 + \alpha(T - 300)]/(1 - \chi P)$$

with the χ and α coefficients regarded as constant and given in the table, the volume V_G^0 being taken at room temperature (300 K) and under atmospheric pressure (chosen as zero pressure).

In the visco-elastic phase, a parabolic shape fits the $P-T$ curves and leads to a $P-V-T$ equation of state which is of first degree in volume and temperature and of second degree in pressure, i.e.

$$V_{ve} = V_{ve}^0[1 + \alpha(T - T_G^0)]/(1 + AP + BP^2)$$

Therefore the isothermal compressibility coefficient χ and thus the slopes of the thermobarograms, in visco-elastic phases cannot be considered as constant (Figs. 1 and 3). The pressure dependence of the volume is expressed as a rational fraction that allows this equation of state to be compared to those proposed in the literature [6]. The values of the constants A, B and T_G^0, and of the coefficient α, regarded as a constant, are given in the table. The volumes V_G^0 and V_{ve}^0 can be determined separately or simultaneously from particular conditions $(P_i-V_i-T_i)$ and from the relation between the phase volumes in both phases at the glass transition temperature under atmospheric pressure:

$$V_{ve}^0 = V_G^0[1 + \alpha(T_G^0 - 300)]$$

For both equations of state, the temperature T is given in kelvins and the pressure P in megapascals.

The curves calculated with the previous equation of state fit the experimental data for both phases well. Examples of theoretical isochoric $P-T$ curves obtained for different V/V^0 ratios are given in Fig. 3(a), (c) and (d) for the three polystyrene materials.

Phase diagrams

The glass transition temperatures T_G extrapolated on thermograms under atmospheric pressure and on thermobarograms under pressure (intersections of the extensions of the curves of both full phases) are reported in Fig. 3 and allow the boundary curves to be drawn between both visco-elastic and glassy phases [5]; for the temperature and pressure ranges studied, these curves can be considered as straight lines. The T_G temperatures obtained from the points of intersection of the equation-of-state curves fit the experimental data very well.

Although the glass transition cannot be considered as second order [7], the slope of the boundary line under various pressures is generally [8] obtained through Ehrenfest's relation [9]

$$\left(\frac{dP}{dT} \right)^E = \frac{\Delta \alpha}{\Delta \chi}$$

where $\Delta \chi$ and $\Delta \alpha$ are respectively the changes for the isothermal compressibility and isobaric expansion coefficients at the glass transition. Other authors (see ref. 10 for several other references) have shown that this relation is not valid and have concluded that the glass transition is not determined by the free volume but rather by the configurational entropy or energies [11]. Calculated and experimental data under atmospheric pressure for the slope $(dP/dT)^E$ are reported in the table. Although the orders of magnitude between both calculated and experimental data are similar for PSK and PSCH, significant differences exist for PSN. Thus Ehrenfest's relation is not always satisfactory in this case, and its use in the determination of the state of a polymer at a given pressure and temperature may lead to erroneous conclusions. Therefore the free volume theory does not appear to explain satisfactorily the phase behaviour of the polymers studied, especially PSN.

Thermodynamic data

Concerning the specific volume V, the introduction of polybutadiene nodules in a standard PS leads to a 8.6–10% mean lowering, depending on the pressure or temperature range; the introduction of carbon black in the "shock" PS yields a 13.5–15% mean increase (Figs. 1 and 2). Table 1 shows that the composition has an effect on χ and α that is opposite to the effect on the specific volume. No real influence is observed for the α/χ ratio or for the slope of the boundary line $(dP/dT)^E$. However, as regards the three polystyrenes studied, for pressures lower than 50 MPa, the lowest T_G values are always observed for the "shock" compound and the highest T_G are always obtained for the standard compound.

The curvature of the thermobarograms is related to the heat capacity at constant volume C_V by the relation

$$\left(\frac{d^2P}{dT^2}\right)_V = \frac{1}{T}\left(\frac{dC_V}{dV}\right)_T$$

For the glass phases of each studied polystyrene, the curvatures can be assumed to be zero, which shows that the C_V changes versus the volume at constant temperature can be neglected over the entire studied range of phase stability. However, along the glass transition, the curvature is positive and the heat capacity C_V must increase when increasing the volume. In contrast, in the visco-elastic phase, the heat capacity C_V decreases when increasing the volume.

The slopes of the thermobarograms for the different phases appear in the explicit expressions of the internal energy [12]

$$E = E^0 + C_V^0 \, dT + \left[T\left(\frac{dP}{dT}\right)_V - P\right] dV$$

and of the entropy

$$S = S^0 + \left(\frac{C_V^0}{T}\right) dT + \left(\frac{dP}{dT}\right)_V dV$$

and give the volume dependence of E and S.

CONCLUSION

P–V–T measurements of the three polystyrene materials were determined by BDA, TBA and DSC. Except for the isothermal compressibility in the visco-elastic phase, the thermodynamic coefficients of the different phases can be considered as independent of pressure and temperature. Simple equations of state were deduced from experimental data in both the glassy and visco-elastic phases. The P–T phase diagrams were determined; in the pressure and temperature ranges studied, the boundary curves are straight lines whose slopes cannot always be obtained by means of Ehrenfest's relation. The composition has a significant influence on the specific volume, isobaric expansion and isothermal compressibility coefficients. These results give information on the phase behaviour of industrial polymers under pressure, which supplies important data for industrial working-up operations.

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