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THERMOELASTIC BEHAVIOUR OF AMORPHOUS POLYMERS ABOVE AND THROUGH THE GLASS TRANSITION INTERVAL

I. Polystyrene

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Abstract

The thermoelastic behaviour of an unfractionated polystyrene was studied in the temperature interval 353–453 K in the regimes of isobaric cooling and of isothermal quasi-adiabatic loading, respectively. The main experimental results can be summarized as follows.

1. In the temperature interval far above the glass transition temperature T_g, both the temperature and volume relaxations of the polystyrene melt after sudden pressure jumps were completely reversible and proved to be simple exponential functions of the time. Therefore, by a straightforward application of Eqs (1) and (2) to the relevant thermoelastic data obtained in a single experimental run one can arrive at the reasonable values of the specific volume, specific heat capacity, thermal diffusivity and heat conductivity of the polymer in the equilibrium melt state.

2. In the temperature interval close to T_g, both the temperature and volume relations of the supercooled polystyrene melt in compression/expansion cycles became markedly asymmetric and non-exponential. The low values of the exponent β in the fractional-exponent Eq. (5) for the volume relaxation suggest a broad spectrum of relaxation times indicating the high degree of coupling between different mechanisms of the molecular motions involved.

Keywords: glassy state, melt state, thermal diffusivity, thermoelastic effect, volume relaxation

Introduction

The thermoelastic effect (i.e., the reversible absorption/release of heat by an elastic body after its sudden external loading/unloading) was predicted theoretically by Thompson [1] to obey the following basic equation:

$$(\partial T/\partial P)_s \cong (\Delta T/\Delta P)_s = (\partial v/\partial T)_p T/c_p \qquad (1)$$

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where v, T, P and S have their usual meanings of specific volume, absolute temperature, pressure and entropy, $(\partial v/\partial T)_P$ and c_P are the (isobaric) specific thermal expansivity and specific heat capacity, respectively.

Starting from the classical studies of Joule [2], the overwhelming majority of experimental tests of the (appropriately modified) Eq. (1) was done on solid polymers and/or rubbers subjected to the uniaxial stretching/contraction (e.g., [3–7]) or to the simple shear [8–10] loading regimes. In contrast, experiments involving application of hydrostatic pressure as explicit in Eq. (1) were relatively scarce both for solid polymers (e.g., [11]) and for polymer melts [12–15]. This is somewhat surprising, in so far as not only the elusive melt c_P at high pressures can be estimated in a straightforward manner by Eq. (1), but also the thermal diffusivity a can be calculated from the exponential decay of temperature increment ΔT with time [12–15]. Combined with simultaneous measurements of specific volume v, these experiments thus permit, finally, to arrive at the heat conductivity as $\lambda = c_P a/v$.

Up till now, this method was used to obtain the cited thermophysical properties of different polymers in the equilibrium melt state (i.e., well outside the temperature and pressure ranges of melt solidification by crystallization and/or glass transition mechanisms) [12–17]. It would be interesting, however, to study the evolution of the thermoelastic response of amorphous polymers in the course of their approach to the glass transition interval. In this first paper of the present series, the relevant experimental data are reported for polystyrene.

Experimental

Cylindrical samples (height and diameter $20\cdot10^{-3}$ and $8.5\cdot10^{-3}$ m, respectively) of an unfractionated linear polystyrene ($<M_n> = 1.2\cdot10^5$, $<M_w> = 3.5\cdot10^{-5}$) were prepared by hot-pressing at 473 K. The glass transition temperature (T_g) of samples prepared in this fashion (determined at normal pressure by calorimetry at a heating rate of 2 K min^{-1}) was 365 K.

The experimental set-up (commonly referred to as the 'thermoelastometer') was described in detail elsewhere [13–16], therefore only essentials will be mentioned here. A polymer sample is placed at room temperature into the pressure chamber which is equipped with a shielded micro-thermocouple located at the geometrical centre of the latter. This inner thermocouple is connected differentially to the identical reference thermocouple fixed in the body of the pressure chamber close to its inner surface. The differential signal between the two thermocouples is converted into the corresponding temperature difference ΔT (the estimated mean error is $1.12\cdot10^{-2}$ K [13–15]).

The experiments were carried out in two alternative regimes. In the regime of isobaric cooling, the sample was heated to T_0=473 K at the nominal pressure P_0= 30 MPa, stored for 15 min to erase the previous structural memory of the polymer, loaded to a predetermined pressure $P_i=P_o+\Delta P_i$ (where $\Delta P_1=10$ MPa, $\Delta P_2=20$ MPa, and so on) and then cooled step-like to $T=353$ K. After keeping for 5 min at each step the isochronal values of the polymer specific volume v_{isot} were calculated (estimated mean error about 0.15%) from the known mass and geometrical dimensions of the sample (with appropriate corrections for pressure and temperature dependencies of the pressure chamber) [13–15]. As can be seen from Fig. 1, each specific volume isobar is reasonably approximated by two linear segments with different slopes $(\partial v_{isot}/\partial T)_P$ which intersect at the apparent T_g. The pressure derivative $dT_g/dP=0.33$ K MPa estimated from Fig. 1 compares well with similar data available for polystyrene [18].

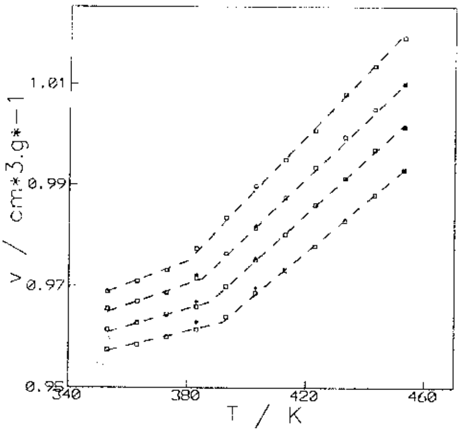

Fig. 1 Temperature dependencies of v_{isot} (squares) and of v_∞ (asterisks) at pressures (from the top downwards): 30, 40, 50 and 60 MPa

In the regime of isothermal loading, the sample was heated again to $T_o=473$ K at the nominal pressure $P_o=30$ MPa, stored for 15 min to erase the previous structural memory, cooled to a predetermined temperature T_i, equilibrated during 15 min and then 'instantaneously' loaded by a pressure increment ΔP_i. After completion of the contraction cycle (associated with the levelling-off and subsequent apparent invariance of readings for the sample height, h_∞, and for the ΔT baseline at $P_i=P_o+\Delta P_i$), the sample was unloaded by a decrement ΔP_i, and the reverse (expansion) cycle was recorded. During relaxation at each temperature and pressure, the time-dependent values of the specific volume v_t of the polymer were calculated as described above.

Thermal diffusivities a in both the loading and unloading cycles were obtained (estimated mean error 3.3%) from the best fits of the descending tails of experimental ΔT_i *vs.* time t curves to the exponential expression [12, 19]

$$\Delta T_t \sim \exp[-(A+BF_{oR})] \qquad (2)$$

where $F_{oR}=at/R^2$ is the Fourier number, $2R$ is the inner diameter of the pressure chamber, A and B are numerical parameters.

Results and discussion

Temperature interval $T \gg T_g$

As can be seen from Fig. 2a, at T=453 K (i.e., far above T_g) the magnitude of the ΔT_i jump increases with increasing ΔP_i; moreover, the patterns of the ΔT_t *vs.* t curves during the unloading cycle (sample expansion) are nearly exact mirror images of the corresponding curves in the loading (sample compression) cycle.

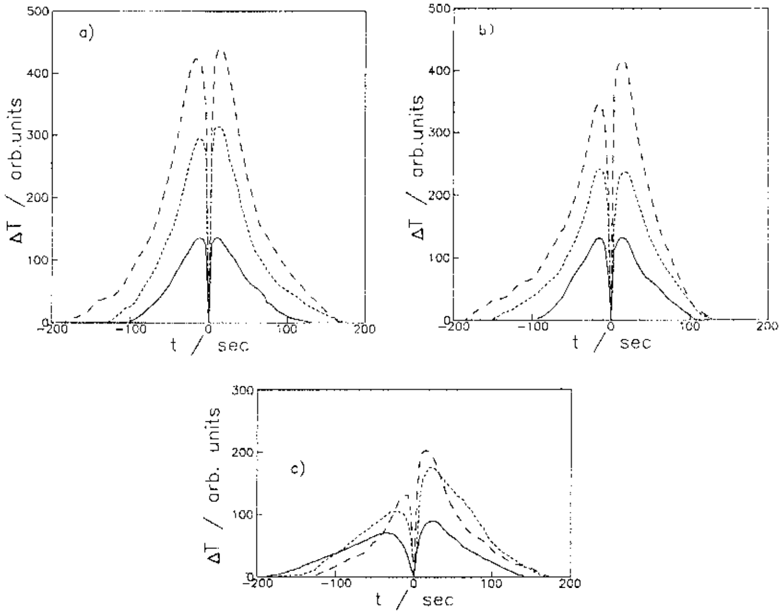

Fig. 2 Time dependencies of ΔT_i in compression (t>0) and in expansion (t<0) cycles at 453 (a0), 403 (b) and 383 K (c) after pressure jumps of 10 (solid lines), 20 (dotted lines) and 30 MPa (broken lines)

The latter observation holds also for the reduced specific volume changes, $\delta_t = (v_o - v_t)/(v_o - v_\infty)$, (Fig. 3a) (here v_o and v_∞ are the specific volumes of the polymer at pressures P_o and $P_i=P_o+\Delta P_i$, respectively). As can be inferred from Fig. 3, the total δ_t may be represented as the sum of two contributions,

$$\delta_t = \delta_{inst} + \delta_{relax} \tag{3}$$

where δ_{inst} is the instantaneous (solid-like) contribution, and δ_{relax} is the time-dependent, relaxational (liquid-like) contribution. At T=453 K the contribution of

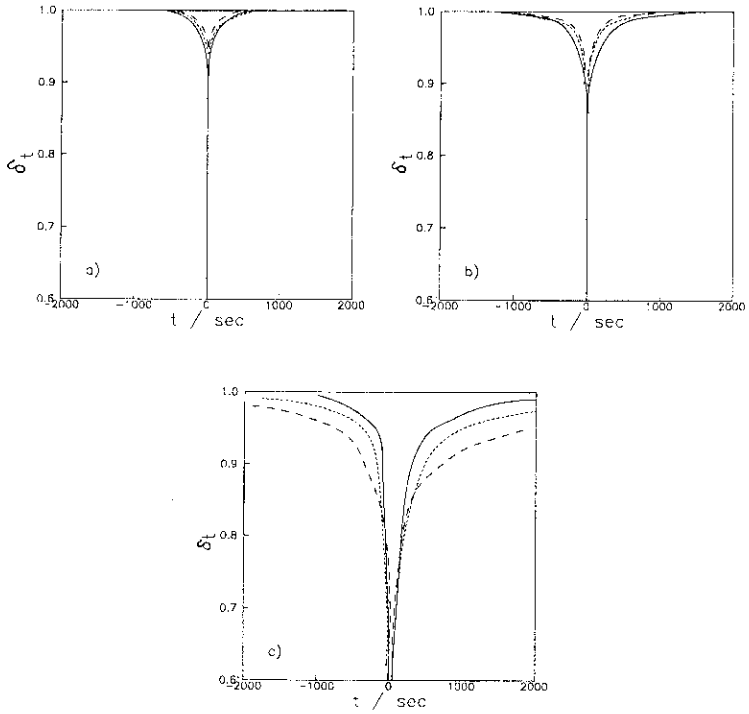

Fig. 3 Time dependencies of δ_t in compression (t>0) and in expansion (t<0) cycles at 453 (a), 403 (b) and 383 K (c) after pressure jumps of 10 (solid lines), 20 (dotted lines) and 30 MPa (broken lines)

δ_{inst} makes over 90% of the total δ_t (Fig. 3a); it can also be shown that the time dependence of the remaining small relaxational contribution is adequately accounted for by a simple exponential function,

$$\delta_{relax} = (\nu_t - \nu_\infty) / (\nu_0 - \nu_\infty) \sim \exp(-t/\tau) \qquad (4)$$

where τ is the relevant relaxation time.

All the above features were observed in a fairly broad temperature interval 473–413 K. It can thus be concluded that each isobaric property in this temperature interval (such as the isochronal specific volumes in Fig. 1) corresponds to the equilibrium state of polystyrene melt characterized by a complete reversibility of structural changes concomitant to the external perturbations (pressure changes). In fact, the final values of ν_∞ by the end of each isothermal relaxation were identical to the values of ν_{isot} obtained in the isobaric cooling regime (Fig. 1).

At each ΔP_i the descending tails of the ΔT_i *vs.* t curves fitted reasonably well to Eq. (2) (Fig. 4); it would be fair to state that the values of thermal diffusivity a

derived from these fits for both the contraction and expansion cycles (Table 1) did not exhibit clear-cut dependence on ΔP_i and fluctuated around the average value $a=(8.2\pm0.4)\cdot10^{-8}$ m^2 s^{-1}. Similar values of thermal diffusivities for polystyrene melts were reported by others [12, 20].

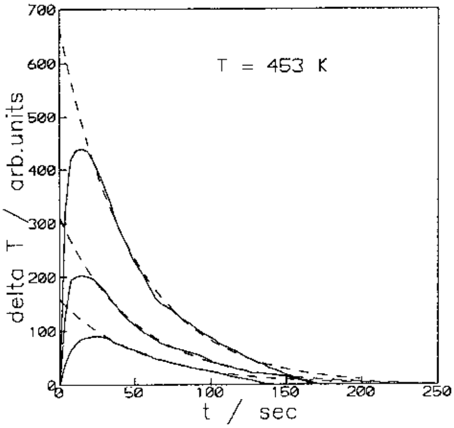

Fig. 4 Experimental (solid lines) and corrected (broken lines) ΔT_i curves at T=453 K after pressure jumps (from the top downwards) of 10, 20 and 30 MPa

As can be seen from Figs 3a and 4, the experimental ΔT_i *vs.* t curves pass through peaks not at t=0 as expected from the theory but after some finite time lag. Moreover, the specific heat capacities c_p calculated by substituting the experimental values of ΔT_i, ΔP_i and $(\partial v_{isot}/\partial T)_P$ (Fig. 1) into Eq. (1) were widely different from tabulated values [18]. Both these features, most probably, should be attributed to the violation of the adiabaticity condition due to uncontrolled heat losses through the thermocouple wires, as was the case with similar data for solutions of oligostyrene [21]. Empirically, the contribution of these effects should be minimized by a substitution of corrected values of ΔT_i (obtained by extrapolation of theoretical exponential curves in Fig. 4 to t=0) into Eq. (1). In fact, by use of this empirical correction the agreement between calculated and tabulated values of c_p at T=453 K could be significantly improved (Fig. 5). The values of heat conductivity calculated as $\lambda=c_p a/v_{isot}=(0.14\div0.18)$ W m^{-1} K^{-1}, also compared well with the available data [18]. Neglecting for a moment the observed scatter of the values of a (Table 1) and of c_p (Fig. 5) derived with this technique, one can argue that λ should increase with the pressure due to a systematic decrease of v_{isot} (Fig. 1).

Temperature interval $T\geq T_g$

As can be seen from Figs 2b and 3b, the ΔT_i *vs.* t and δ_t *vs.* t plots at T=403 K remain symmetrical in contraction/expansion cycles at $\Delta P_i\leq2020$ MPa, whereas

Table 1 Parameters of the temperature and volume relaxations of polystyrene in the isothermal loading regime

ΔP_i	a/ 10^8m^2 s^{-1}	Δh_{exp}/	Δh_{trial}/	t_{exp}/	t_{trial}/	β
		arb. units		min		
			T=435 K			
+10/–10	7.74/8.59	–	–	–	–	–
+20/–20	8.44/7.98	–	–	–	–	–
+30/–30	7.76/8.71	–	–	–	–	
			T=405 K			
+10/–10	8.94/8.86	–	–	–	–	–
+20/–20	8.98/8.97	–	–	–	–	–
+30/–30	9.51/9.12	–	–	–	–	–
			T=383 K			
+10/–10	–	90/65	91/66	35/16	357/35	0.26/0.36
+20/–20	–	185/144	187/145	86/44	2358/1820	0.20/0.22
+30/–30	–	226/219	228/220	93/155	17320/885	0.17/0.27

it is only at the highest pressure increment (ΔP_3=30 MPa) that a marked asymmetry sets in. The latter feature (i.e., the asymmetry of such plots in contraction/expansion cycles) became much more pronounced when the temperature was lowered further to T=383 K (Figs 2c and 3c); moreover, the contribution of the δ_{relax} was observed to increase to about 40% of the total δ_t. Finally, one could also observe gradual positive deviations of the apparent values of v_∞ in this temperature interval from the linear isobars for equilibrium values of v_{isot} at higher temperatures (Fig. 1).

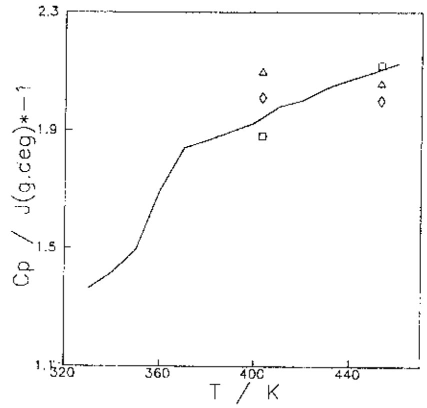

Fig. 5 Tabulated (solid line) and calculated values of c_p obtained at ΔP_i=10 (squares), 20 (triangles) and 30 (diamonds) MPa

As can be estimated from Fig. 1, $T_g \cong 378$ K and 389 K at $P_o=30$ MPa and at $P_3=P_o+\Delta P_3=60$ MPa, respectively. Based on these estimates, it seems reasonable to attribute the characteristic features of the ΔT_i *vs.* t, δ_t *vs.* t and v_∞ *vs.* T plots referred to above the drastic slowing down of molecular motions (hence, incomplete structural relaxation) of the polystyrene melt during its excursions into and out of the (pressure-induced) glass transition intervals.

It could be easily verified that the time dependencies of the δ_{relax} contributions (Figs 3b, 3c) no longer obeyed Eq. (4); therefore, an attempt was made to fit the experimental data to the fractional-exponent relationship (e.g., [22, 23]),

$$\delta_{relax} \sim \exp(-t/\tau)^{\beta} \quad (5)$$

where $0<\beta<1$ is the phenomenological measure of the width of the relaxation times spectrum.

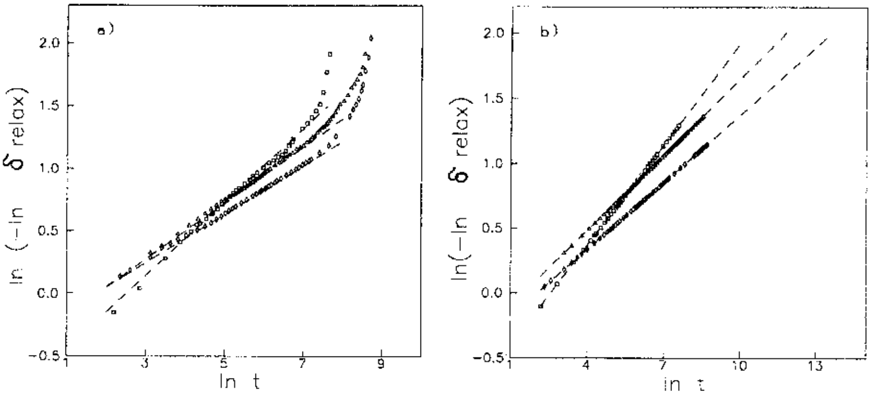

Fig. 6 Initial (a) and corrected (b) $\ln(-\ln\delta_{relax})$ *vs.* $\ln t$ plots at $T=383$ K after pressure jumps of 10 (squares), 20 (triangles) and 30 (diamonds) MPA (compression cycle)

As can be seen from Fig. 6a, the expected linearity of the $\ln(-\ln\delta_{relax})$ *vs.* $\ln t$ plots was limited only to the initial stages of relaxation processes if the values of v_∞ were assumed to correspond to the apparent levelling-off of the sample height change Δh_{exp} after a time interval of t_{exp} (Table 1). It turned out, however, that relatively minor corrections to the v_∞ by replacement of Δh_{exp} by appropriately chosen trial values Δh_{trial} (Table 1) resulted in linearity of the $\ln(-\ln\delta_{relax})$ *vs.* $\ln t$ plots over the entire experimental time interval t_{exp} (Fig. 6b). As could be expected, in all cases the exponents β calculated from the slopes of linear plots were well below unity (Table 1) which is an indication of the high degree of coupling between different mechanisms of the molecular motions involved [22–24].

Incidentally, the quasi-equilibrium values of v_∞ derived in this fashion were close to (but still above) the theoretical isobars obtained by a linear extrapolation of the equilibrium values of v_{isot} from high temperatures (Fig. 1). However, the giant differences between the experimental and expected values of the time interval for completion of the relaxation processes (t_{exp} and t_{trial} in Table 1, respectively) concomitant to the relatively insignificant differences between corresponding Δh_{exp} and Δh_{trial} were in fact remarkable. These differences give a feeling of a precipitous slowing down of the approach of a polystyrene melt to a new equilibrium structure, when it deeply penetrates the glass transition interval.

Conclusions

1. In the temperature interval far above T_g, both the temperature and volume relaxations of the polystyrene melt after sudden pressure jumps were completely reversible and proved to be simple exponential functions of the time. Therefore, by a straightforward application of Eqs (1) and (2) to the relevant thermoelastic data obtained in a single experimental run one can arrive at reasonable values of the specific volume, specific heat capacity, thermal diffusivity and heat conductivity of the polymer in the equilibrium melt state.

2. In the temperature interval close to T_g, both the temperature and volume relaxations of the supercooled polystyrene melt in compression/expansion cycles became markedly asymmetric and non-exponential. The low values of the exponent β in the fractional-exponent Eq. (5) for the volume relaxation suggest a broad spectrum of relaxation times indicating the high degree of coupling between different mechanisms of the molecular motions involved.

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