Journal of Thermal Analysis Vol. 46 (1996) 973-983

Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

ISOTHERMAL AND ISOBARIC PVT-MEASUREMENTS OF ANIONIC POLYSTYRENES

'Relaxation zones' within the glass transition range

*A. Eckstein and H. A. Schneider**

Institut für Makromolekulare Chemie "Hermann-Staudinger-Haus"
*Freiburger Materialforschungszentrum, FMF, der Universität, Stefan-Meier-Strasse 21,
D-79104 Freiburg, Germany

Abstract

PVT-measurements of anionic polystyrenes on heating have shown that, depending on the mode of operation, specific 'relaxation zones' within the glass transition range are observed. Isothermal PVT curves exhibit always 'relaxation zones' independent whether the pressure is increased or decreased during the scan. The shift of the relaxation zones to higher temperatures is, however, higher for isothermal scans with increasing pressure. These 'relaxation zones' are explained by pressure-dependent changes of the state of the polymeric sample isothermally scanned within the glass transition range. At lower pressures the polymer is actually in the molten state, whereas at higher pressures it may be in the metastable glassy state and the actual state depends on the rate of pressure change. In isobaric PVT curves 'relaxation zones' in heating scans are exhibited only if the pressure applied during glass formation differs from the pressure applied during the heating scan. The observed pressure-dependent shift of the glass temperatures to higher temperatures was higher for the studied polystyrenes of different molecular weight that had a higher glass temperature at normal pressure. But the specific molecular weight influence on the width of the 'relaxation zone' could not be ascertained. An attempt to calculate characteristic volume relaxation times failed because of insufficient precision of the measurements.

Keywords: isothermal and isobaric PVT, molecular weight dependent pressure influence on T_g, PVT of anionic polystyrenes, T_g relaxation dependence

Introduction

Oels and Rehage [1] have concluded, based on results of PVT-measurements for atactic polystyrenes, that the glass transition of polymers is a freezing-in process which can be characterized thermodynamically by one additional internal ordering parameter. As a consequence, glass transitions are characterized by relaxation phenomena, noticeable in PVT-diagrams during heating through the glass transition range by a given zone of more or less stationary, or even decreasing volume. According to Zoller and Hoehn [2] the width of this volume

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

relaxation zone shown by the heating PVT-curves is enlarged by increasing the pressure. Quach and Simha [3] have explained the volume relaxation zone by the transition back to the glassy state when the melt is pressurized, the exact location depending on the rate at which pressure is applied. Based on thermal analysis data and dilatometric measurements, Weitz and Wunderlich [4] have pointed already in 1974 at the occurrence of a significant volume relaxation during depressurization of polymers in the glass transition range.

Although the relaxation phenomenon is always observed in heating PVT-scans of amorphous polymers covering the glass transition range, (see also [5]), to our knowledge none of the published papers are concerned with the effect of the mode of operation on the relaxation zone. In a previous study about the influence of pressure on the glass transition of amorphous polymers we have shown that both the glass temperature and the width of the relaxation zone increase more with pressure the higher the glass temperature of the polymer at atmospheric pressure [5]. In this paper we present data concerning the influence of the mode of operation used in PVT-measurements on both the glass transition temperature and the belonging relaxation zone of amorphous polystyrenes taking into account both the molecular weight and the history dependence of glass transition.

Experimental

Five polystyrenes obtained by anionic polymerization were used for the PVT-measurements. The molecular weights and the provenances of the PS samples are presented in Table 1.

Table 1 Polystyrenes used for the PVT-measurements

Polymer	PS 2[a]	PS 5[a]	PS 20[b]	PS 55[a]	PS 1.2Mio[c]
M_w/g mol^{-1}	2 300	5 000	20 000	54 000	1200 000
M_n/g mol^{-1}	2 100	4 200	18 800	51 000	1130 000
M_w/M_n	1.09	1.19	1.06	1.05	1.06

[a] Obtained from BASF,
[b] by anionic polymerization in THF,
[c] obtained from Aldrich M_w and M_n determined by GPC

The PVT-measurements were carried out using the commercial GNOMIX PVT apparatus based on principles discussed in detail by Zoller *et al.* [7]. The polymer sample (~ 1 g) is placed under vacuum together with mercury as a confining fluid in a rigid piezometer cell closed off at one end by a flexible bellow. The linear deflection of the bellow due to expansion or contraction of both the sample and the confining fluid is measured by a variable differential transducer and is converted, after calibration, to the respective volume changes of the sample. The piezometer cell is placed inside a pressure vessel in which temperatures from room temperature up to 400°C and pressures to 200 MPa can be maintained. For PVT-measurements different isothermal and isobaric modes of operation can be chosen.

In the isothermal mode of operation the pressure can be either increased in steps of 10 MPa from 10 MPa to 200 MPa or decreased from 200 MPa to 10 MPa. The respective values of the specific volume for 0 MPa are obtained by extrapolation.

In the first isobaric mode of operation used, the melt was every time relaxed to the pressure of 10 MPa and then cooled down at a constant cooling rate. The glass obtained at 10 MPa was then compressed to the pressure of the next isobaric scan and the volume changes were measured during heating of the glass using a constant heating rate. In the second isobaric mode of operation the melt was first compressed to the pressure of the next isobaric heating scan and then cooled. The volume changes of the glass obtained at the pressure of measurement were then recorded by heating the sample at a constant heating rate. In both modes of operation the cooling and heating rates were 4 K min^{-1}.

Results and discussion

The glass transition of a polymer is usually characterized in isobaric PVT-measurements by a sharp bend of the *V–T* curve, provided the polymer is cooled from the equilibrium melt into the glass at constant cooling rate. If the volume changes are measured during heating of a 'frozen-in' metastable glass, in contrast, pressure induced relaxation zones are observed in the glass transition range in both isothermal and isobaric modes of operation. As mentioned in the introduction, these relaxation zones are clearly demarcated in the respective

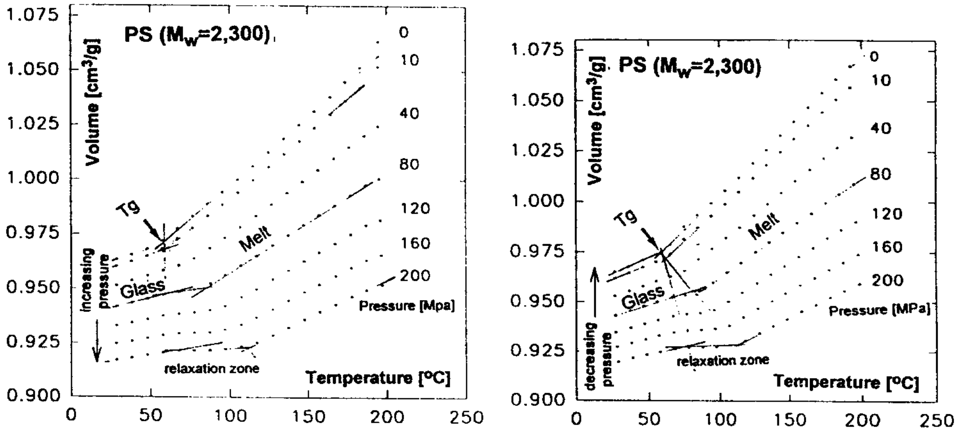

Fig. 1 Isothermal PVT-diagrams of polystyrene, PS 2 (M_w=2 300) scanned starting from the glassy state by a) stepwise decreasing and b) increasing pressure

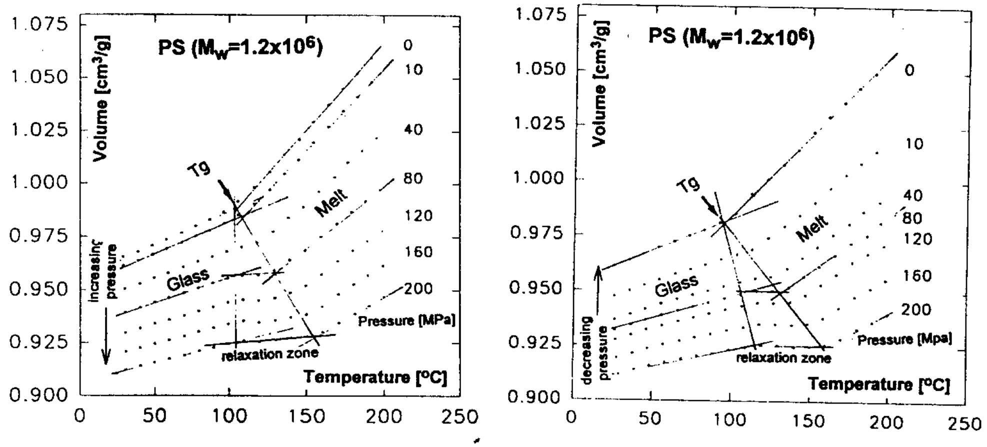

Fig. 2 Isothermal PVT-diagrams of polystyrene, PS 1.2 Mio ($M_w=1.2\times10^6$) scanned starting from the glassy state by a) stepwise decreasing and b) increasing pressure

PVT-diagrams (extending over temperature ranges up to 60 K dependent on the pressure), because the volume is either almost constant or, sometimes, even decreasing with increasing temperature.

In the isothermal mode of operation the width of the relaxation zone depends evidently on the direction of the pressure change used in the mode of operation, i.e. whether the pressure is decreased stepwise or increased during the isothermal volume measurements. This is demonstrated for example by the respective PVT-diagrams shown in Fig. 1 for PS 2 and Fig. 2 for PS 1.2 Mio. Generally the 'relaxation zone' is shifted to higher temperatures when the pressure is decreased during the isothermal scan. The effect is relatively small, as can be seen from Fig. 3 for PS 55, were the PVT diagrams obtained by the isothermal mode

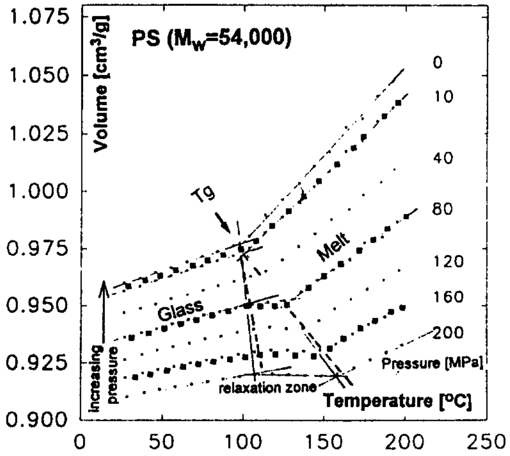

Fig. 3 Superimposed isothermal PVT-diagrams of PS 55 scanned starting from the glassy state. Points – for stepwise increasing pressure, squares – for decreasing pressure

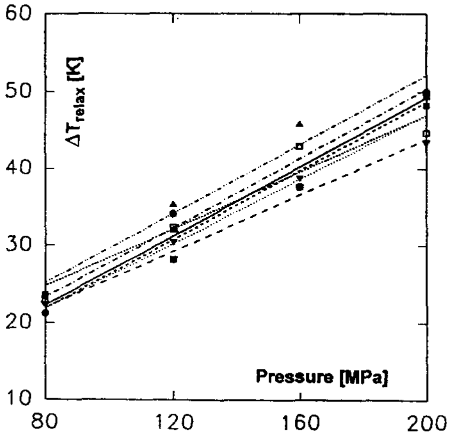

Fig. 4 Pressure dependence of the width of the 'relaxation zone', ΔT_{relax}, observed in the PVT-diagrams scanned during the isothermal mode of operation filled symbols - data obtained by increasing pressure, open signs - data obtained by decreasing pressure; •, ▿ - PS 2; ▴ - PS 20; ▾, □ - PS 55 and ▪, ▵ - PS 1.2 Mio

of operation with increasing and decreasing pressure are superimposed. For clarity the isothermal PVT data for decreasing pressure are shown only for 10, 80 and 160 MPa.

The influence of the molecular weight on the width of the relaxation zone is less. This is confirmed by the data shown in Fig. 4, where the pressure dependence of the width of the relaxation zones, ΔT_{relax}, defined by the difference $(T_g-T_l)_P$, is illustrated. T_l represents the temperature at which the further volume increase of the glass stops (it is marked by the low temperature line delimiting the relaxation zones in the PVT-diagrams). Although the relaxation zones are delimited for clarity by straight lines in Figs 1–3, a tendency of leveling off of T_l and even more for T_g with increasing pressure is observed. From the data shown in Fig. 4, except of an overall enlargement of the relaxation zone with increasing pressure, neither an influence of the direction of the pressure change during the isothermal scans, nor of the molecular weight on the width of the relaxation zone can be safely ascertained. The reduced volume increase (or even decrease) within the relaxation zone can be ascribed on the one hand to density changes and on the other hand to volume relaxations due to the metastability of the frozen-in polymeric glasses.

The pressure dependence of the glass temperatures, T_g, of the studied PS samples were estimated from the PVT-diagrams obtained by the isothermal mode of operation for both increasing and decreasing pressure during the isothermal scans. As it results from the data shown in Fig. 5 the tendency of leveling off of the glass temperature with increasing pressure is obvious. This confirms the results of Sasuga and Takehisa [8], who have shown that the pres-

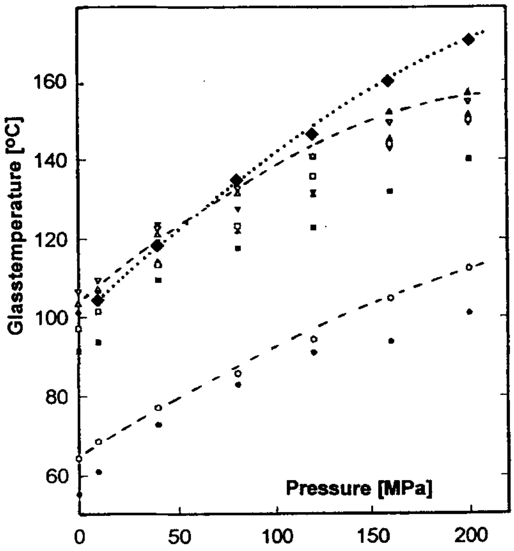

Fig. 5 Pressure dependence of the glass temperatures of polystyrenes measured from PVT-diagrams obtained by the isothermal mode significance of filled and open symbols as in Fig. 3, ●, ○ - PS 2; ■, □ - PS 5; ▲, △ - PS 55 and ▼, ▽ - PS 1.2 Mio ◆ - PS 1.2 Mio, isobaric mode of operation

sure dependence of the glass temperature can be described by a second power equation in pressure with a negative coefficient of the second power term. The diminution of the increase of the glass temperature with increasing pressure is evidenced also by other methods of investigation [9].

On the other hand, it seems that the pressure-influence intensifies with increasing glass temperature at atmospheric pressure of the polystyrenes of different molecular weights (see dashed lines in Fig. 5 for PS 2 and PS 1.2 Mio, respectively). This is also confirmed by the pressure dependence of the difference between the glass temperatures of PS 1.2 Mio and PS 2. The respective mean values of these temperature differences, ΔT_g, observed in the isothermals mode of operation are listed in Table 2.

The shapes of the PVT-curves obtained by the isobaric modes of operation change dramatically with the conditions used for the glass formation by cooling of the polymer melt, as it results from the diagrams shown in Fig. 6. Whereas isobares scanned during heating cycles of the polymeric glasses resulted after cooling of the melt at 10 MPa exhibit clearly relaxation zones in the glass tran-

Table 2 Pressure dependence of the difference between the glass temperatures of PS 1.2 Mio and PS 2

Pressure/MPa	10	40	80	120	160	200
$\Delta T_g = T_{g_{1.2Mio}} - T_{g_2}$ /K	40.6	44.8	46.7	46.0	45.6	45.2

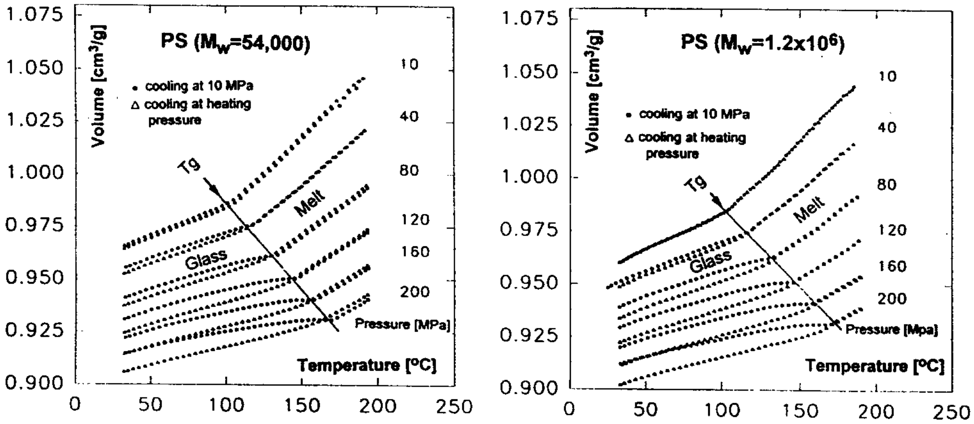

Fig. 6 PVT-diagrams of PS 55 and PS 1.2 Mio obtained by the isobaric mode of operation. Full circles - cooling of the polymer melt at the pressure of 10 Mpa. Open triangles - cooling of the melt at the pressure of the isobaric measurement

sition range, they disappear entirely in the isobaric heating scans of glasses obtained by cooling of the melt at the pressure of measurement. Additional the pressure influence on the glass temperature is much more accentuated in the isobaric then in isothermal scans. For illustration in Fig. 5 are included comparatively the respective glass temperatures of PS 1.2 Mio.

Relaxation zones are thus observed in isobaric PVT-diagrams only if the pressure applied during the formation of the polymer glasses is different from the pressure used in the subsequent isobaric heating scan. The pressure dependence of the width of the relaxation zones observed in the isobaric scans of polymer glasses obtained by cooling of the polymer melt at 10 MPa is illustrated in Fig. 7. Again, no distinct influence of the molecular weight of the studied PS can be ascertained. The width of the relaxation zones observed in the isobaric PVT measurements are, however, by a factor of two smaller than for the relaxation zones observed in isothermal scans.

In conclusion, relaxation zones in the glass transition range are always shown by isothermal PVT heating scans of polymeric glasses. In isobaric PVT heating scans of polymeric glasses, relaxation zones are observed only if the pressure of glass formation was different from the pressure used in the isobaric heating scan.

It is well known that the return of a perturbed system to thermodynamic equilibrium is characterized by relaxation, i.e. the recovery of the equilibrium state is time dependent. The volume relaxation of frozen-in glasses above their glass temperature can be described theoretical by the models of Tool [10] and Moynihan [11]. The relaxation model was adapted for polymers by Kovacs *et al.* and is generally known as the KAHR-model [12]. Volume *vs.* time curves

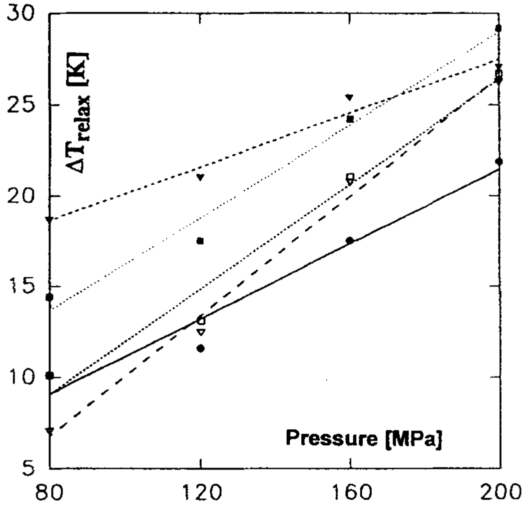

Fig. 7 Pressure dependence of the width of the relaxation zone, ΔT_{relax}, observed during isobaric measurements of polymeric glasses obtained at 10 MPa; • - PS 2, ▿ - PS 5, ▾ - PS 20, □ - PS 55 and ■ - PS 1.2 Mio

observed after perturbation of the system by a pressure relaxation jump are always characterized at the beginning by a strong increase of the volume which is mainly due to the respective sudden pressure decrease. This effect dominates at the beginning the own relaxation of the metastable polymeric glass and as a consequence it is not possible to discern the effective relaxation phenomenon. But the volume change of the polymer continues also after pressure equilibration. This latter volume change can be ascribed to relaxation. The volume relaxation of polymers in the glass transition range after pressure equilibration can be described by the equation of Kohlrausch-Williams-Watt (KWW):

$$v(t) = v_o + \Delta v[1 - \exp(-(t/\tau)^{\beta})] \qquad (1)$$

$v(t)$ is the time dependent volume of the glass, v_o is the initial volume for $t=0$ and Δv is given by the difference $v_f - v_o$, v_f being the final volume for infinite time of observation. Consequently, v_f is experimentally not accessible because of the extremely slow conformational rearrangements of polymers at low temperatures [13]. Finally, t is the experimental time of the observed volume change, τ a characteristic relaxation time and β a measure of the width of the relaxation time spectrum.

For the volume relaxation studies the PS samples have been brought into the liquid state at 200 MPa and 200°C. Then the samples were cooled to the glassy state at 30°C, maintaining the pressure of 200 MPa. The frozen-in glasses at 200 MPa were subsequently isothermally relaxed to 10 MPa and the time-dependent changes of the volume were measured. But our attempt to use the KWW Eq. (1) for evaluation of the characteristic volume relaxation time failed because of the lack of a certain value for Δv (as mentioned, the equilibrium value of v_f for 10 MPa of a polymeric metastable frozen-in glass is experimentally not accessible). By fitting of the experimental volume *vs.* time curves, too large Δv values are obtained. Using these erroneous Δv values to recalculate the volumes of PS, higher specific volumes are obtained for higher then for lower pressures.

In the next attempt of evaluation of the characteristic volume relaxation times, a transformed KWW equation has been used

$$\log(v-v_o) = \log\Delta v - \beta\log\tau + \beta\log t \tag{2}$$

It results from taking of the logarithms and developing of the exponential term, $\exp(-t/\tau)^{\beta}$, into a series and retaining the first term only, taking into account that $t/\tau << 1$. Representing according to this logarithmic equation $\log(v\text{-}v_o)$ *vs.* $\log t$, straight lines should result with a slope β and an intercept $[\log\Delta v - \beta\log\tau]$.

As can be seen from Fig. 8, straight lines are, indeed, obtained, but the scatter of the experimental data is high, higher for higher molecular weights. The mean value of the slopes of the fitted lines shown in Fig. 8 is of $\beta = 0.53 +/- 0.08$ and as a first approximation it can be considered a constant, i.e. independent of the molecular weight. The estimated value of β is in accordance with the values (between 0.2 and 0.6) obtained by Tribone *et al.* for PS [14]. But even knowing the value of β, the characteristic relaxation time can still not be evaluated, because the intercept of the lines depends on both τ and Δv, the latter being, as shown, experimentally not accessible.

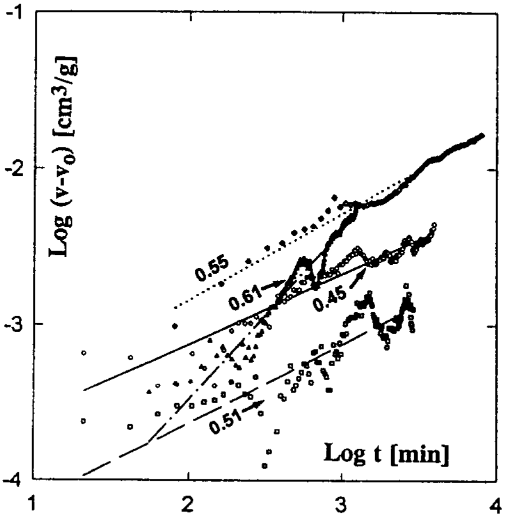

Fig. 8 Time dependent volume relaxation of polystyrenes; ◇ - PS 2, ▲ - PS 5, ○ - PS 20 and □ - PS 1.2 Mio (The numbers indicate the slopes of the respective lines)

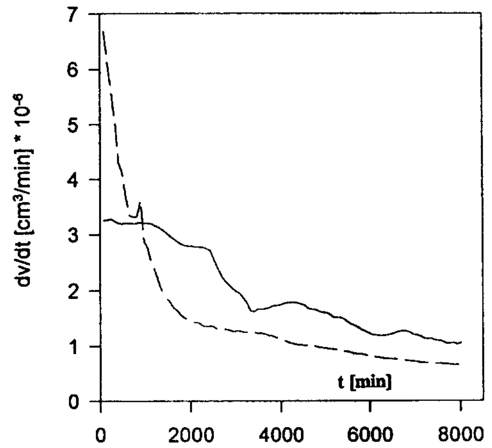

Fig. 9 Experimental volume relaxation and fitted curve, represented according to Eq. (3); Full line - experimental curve, dashed line - fitted curve

Consequently, in a further attempt of estimating the characteristic volume relaxation time, Eq. (2) has been differentiated and the experimentally unaccessible Δv has been substituted in the resulting Eq. by the value given by Eq. (1). The resulting expression is of the form:

$$(dv/dt) = [(v-v_o)(\beta/\tau)(t/\tau)^{\beta-1}\exp(-(t/\tau)^{\beta})] \,/\, [1-\exp(-(t/\tau)^{\beta})] \qquad (3)$$

By fitting procedure, one should be able to estimate the characteristic relaxation time using Eq. (3), because all other factors included in Eq. (3), i.e. v, v_o, t and β, are now known. The result of this last fit is illustrated in Fig. 9. It is evident that the discrepancy between the experimental and fitted curves is too large for an unequivocal determination of the characteristic volume relaxation time of PS. Thus, only after an improvement of the precision of volume relaxation measurements using the GNOMIX PVT-apparatus would it be possible to evaluate the characteristic volume relaxation times of polymeric glasses.

* * *

Acknowledgement is made to the Deutsche Forschungsgemeinschaft (SFB 60) for financial support of this research.

References

1 H.-J. Oels and G. Rehage, Macromolecules, 10 (1977) 1036; G. Rehage, J. Macromol. Sci.-Phys., B18 (1980) 423.
2 P. Zoller and H. H. Hoehn, J. Polymer Sci., Polymer Phys.Ed., 20 (1982) 1385.
3 A. Quach and R. Simha, J. Appl. Physics, 42 (1971) 4592.
4 A. Weitz and B. Wunderlich, J. Polymer Sci., Polymer Phys. Ed., 12 (1974) 2473.

5 T. Ougizawa, G. T. Dee and D. J. Walsh, Polymer, 30 (1989) 1675; J. Kressler, N. Higashida, K. Shimomai, T. Inoue and T. Ougizawa, Macromolecules, 27 (1994) 2448.
6 H. A. Schneider, B. Rudolf, K. Karlou and H.-J. Cantow, Polym. Bull., 32 (1994) 645.
7 P. Zoller, P. Bolli, V. Pahud and H. Ackermann, Rev. Sci. Instrum., 47 (1976) 948.
8 T. Sasuga and M. Takehisa, J. Macromol. Sci.-Phys., B13 (1977) 215.
9 V. F. Skorodumov and Yu. K. Godovsky, Polymer Science, 35 (1993) 562. (translated from Vysokomol. Soedineniya B35 (1993) 214).
10 A. Q. Tool, J. Amer. Ceram. Soc., 54 (1971) 491.
11 M. A. Debolt, A. J. Easteal, P. B. Macedo and C. T. Moynihan, J. Amer. Ceram. Soc., 59 (1976) 16.
12 A. J. Kovacs, J. J. Aklonis, J. M. Hutchinson and A. R. Ramos, J. Polymer Sci., Polymer Phys. Ed., 27 (1989) 837.
13 J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys., 28 (1958) 373, 807.
14 J. J. Tribone, J. M. O'Reilly and J. Greener, J. Polymer Sci., Polym. Phys., 27 (1989) 837.