Thermochimica Acta, 163 (1990) 325–330
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PRESSURE EFFECT ON RELATIONS BETWEEN GLASS TRANSITION TEMPERATURE AND FREEZING-IN RATE FOR POLYSTYRENE

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SUMMARY

Glass transition temperature, Tg, was determined for an anionic polystyrene by using an integral method from DTA data obtained at 0.1 and 400 MPa. Tg decreased as the rate of cooling through the glass transition region was lowered. The gradients over 1 K/h to 20 K/min were 2.24 K/decade at 0.1 MPa and 1.51 at 400 MPa. In order to get an insight in the number of internal order parameters that govern the glassy state, the data were compared with the P-V-T data reported by Oels and Rehage (ref. 15).

INTRODUCTION

In general, the glass transition could be described as a "frozen-in" process for which the ideas of order parameters z were used (refs. 1-3). In a liquid z could be defined as a function of temperature T and pressure P. On cooling the liquid, z was frozen in at a glass transition temperature Tg and remained constant below Tg. We will treat the glass transition in terms of this simple order parameter theory (SOPT).

There have been many controversies on the number of z enough to describe the glassy state. One of them was concerned in the Prigogine-Defay ratio r (ref. 2), defined by

$$r = \Delta Cp \ \Delta\kappa \ /[\ Tg \ Vg \ (\ \Delta\alpha\ )^2\ ] \tag{1}$$

where Vg is volume at Tg, and Cp, κ, α are heat capacity at constant pressure, isothermal compressibility and thermal expansion coefficient, and Δ represents the differences of these properties between liquid and glass. Davies and Jones argued that r=1 for one order parameter, while r>1 for more than one parameter (ref. 1). Because r>1 was found experimentally, more than one z seemed to be required to describe the glassy state. Subsequently controversies on this issue continued (refs. 4-11). Another point was whether transition line $Tg(P|V)$ determined on volume surface $V(T,P)$ was identical or not with $Tg(P|S)$ due to entropy surface $S(T,P)$ [or enthalpy one $H(T,P)$]. We will deal with this issue.

In the references cited above $Tg(P)$ was treated to be determined by the same value of z irrespective of pressure. From an experimental view point, it is easy to control z in terms of the freezing-in rate q at each pressure. There

0040-6031/90/$03.50

are differences in suitable scanning rates for determining Tg by dilatometry and DTA. The latter is generally performed under heating scan, whose rates are faster than in the former. Richardson and Savill reported that Tg could be determined through enthalpy curves transformed from heating DSC data for slowly cooled polystyrene (ref. 12). We confirmed that at atmospheric pressure Tg obtained from cooling dilatometry and DSC was in identical relations against q over 1 K/h to 20 K/min for polystyrene and polymethylmethacrylate, respectively (ref. 13).

In this report the relation between Tg and q for an anionic polystyrene was determined at 400 MPa by using a high pressure DTA (ref. 14), and pressure effect on it was examined. These relations were compared with dilatometric data reported by Rehage (refs. 15,16) in order to get an insight in the number of z that governs the glassy state.

EXPERIMENTAL

Sample

A standard anionic polystyrene F-2 (Batch TS-159) purchased from Toyo Corporation was used. Its specifications provided by the manufacturer showed $Mw = 1.96 \times 10^4$ and $Mw/Mn \simeq 1.01$. Powdered sample was evacuated for 2 hr at 160 °C to eliminate low molecular weight impurities and a pressed sheet was made, from which a measuring sample was punched out.

Apparatus

The details of the high pressure DTA were described in the previous paper (ref. 14). In order to reduce the heat capacity of a sample cup, thermocouple was spot-welded instead of soldering. Sample weight was about 5 to 6 mg. Pressure was calibrated by using a Heise pressure gauge and also a reltion between melting point and P for indium. T and ΔT signals were stored in a personal computer NEC8001-MkII and used for data analysis.

For atmospheric pressure measurements a Rigaku DSC8240 with TAS100 was used.

RESULTS AND DISCUSSION

From SOPT it follows that Tg is defined as an intersection temperature extrapolated from liquid and glassy V-T or H-T relations (ref. 16). Since our high pressure DTA was essentially of heat-flux type (ref. 17), the data could be integrated. Although DTA data also had to be obtained on cooling, thermal noises in the high pressure DTA were larger in cooling scan than in heating. And at slow cooling the jump on DTA curves became ambiguous to determine Tg with enough accuracy. When the scanning rate was relatively high, we could compare DTA curves obtained on both the heating and cooling scan. Fig. 1 shows the results at 400 MPa. The sample was firstly cooled from liquid to glass with 10 K/min

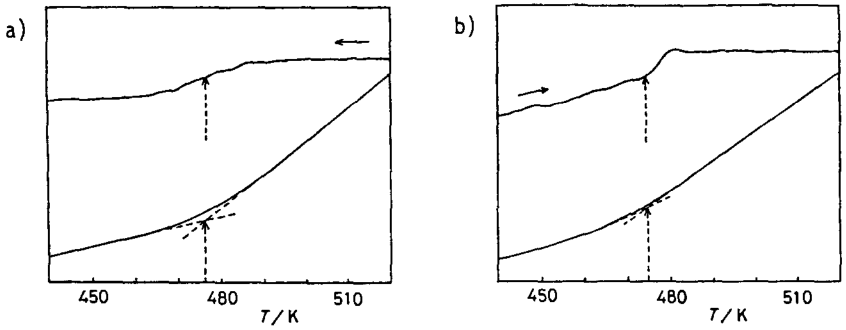

Fig. 1. DTA curves for polystyrene measured at the rate of 10 K/min at 400MPa and their corresponding integral curves. a) cooling and b) heating scan.

and when reached at 60 to 70 K below *Tg* the heating scan was started with the same rate. In addition to the DTA curves obtained the corresponding integral curves are drawn. The *Tg* extrapolated from the integral curve of the cooling scan corresponds to the middle point temperature on the DTA curve. And the *Tg* determined from the heating integral curve approximately coincides with the intersection temperature before the jump on the DTA curve. These findings are similar to those observed at atmospheric pressure. The cooling and heating runs provide different *Tg*, but only by about 2 K. It may be said that under high

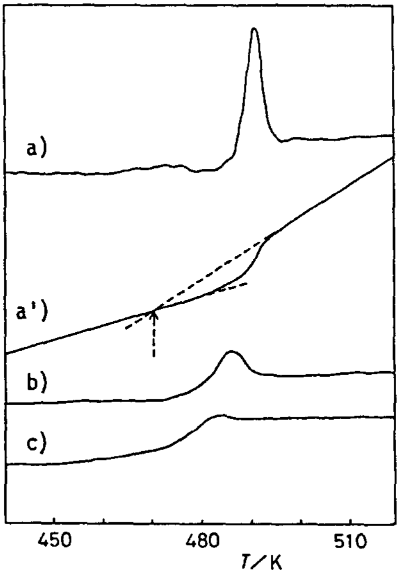

Fig. 2. Comparison of DTA curves for various glasses of polystyrene at 400 MPa. Freezing-in rate: a) 1 K/h, b) 0.5 K/min and c) 20 K/min. Rate of DTA heating scan: 20 K/min. a') integral curve from the curve a), indicating *Tg*

pressure Tg could be determined with enough accuracy from the integral method.

Fig. 2 shows the heating DTA curves measured with 20 K/min for the samples glassified at various freezing-in rates at 400 MPa. As at atmospheric pressure the peaks after the jump on heating DTA curve that are ascribed to super-heating effect become prominent with decreasing in the rate. For the sample frozen at 1 K/h the integral curve is drawn, on which also the super-heating can be seen. The extrapolated Tg very differs from that usually assigned on the DTA curve.

Tg is plotted against logarithm of the freezing-in rate q in K/min in Fig. 3. All the Tg were determined from the integral curves of the heating scan. The data at atmospheric pressure in Fig. 3 a) were obtained by the Rigaku DSC8240. Although there are some scatters over a range of low q, it may be said that a linear relation between Tg and log q hold irrespective of the scan rates. The dotted line represents a relation determined from cooling DSC and dilatometry. Its details will be given elsewhere (ref. 13). Agreement between both relation is good. That Tg of the samples glassified at very slow rate can be determined through the integral method agrees with the finding by Richardson and Savill (ref. 12). The relation is expressed as

$$Tg = A + B \log q \qquad (2)$$

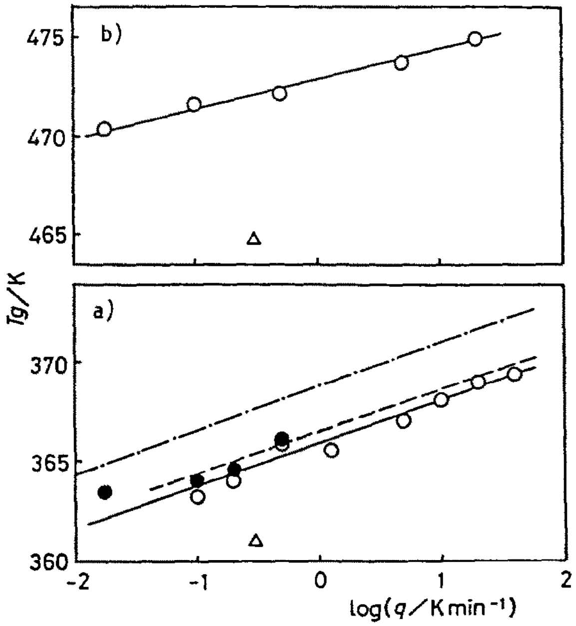

Fig. 3. Pressure dependence of the relation between Tg and freezing-in rate q for polystyrene. a) 0.1 MPa; DSC heating rate: 2 K/min by filled circle, 20 K/min by open circle; dotted line by us (ref. 13), chain line by Richardson and Savill (ref. 12). b) 400 MPa; DTA heating rate: 20 K/min. Triangles in a) and b): dilatometric data by Oels and Rehage (ref. 15).

where q is in the unit of K/min. The constants A and B at atmospheric pressure are given in Table 1. The dotted line gives B = 2.1 K/decade. The chain line represents a relation reported for an anionic polystyrene of $Mw = 3.6 \times 10^4$, whose gradient is 2.2 K/decade (ref. 12). A difference in A of about 2.5 K between the present relation and theirs could be resonably interpreted in terms of the molecular weight dependence (refs. 16,19).

The data at 400 MPa are also represented by a linear relation over 1 K/h to 20 K/min. The values of A and B are also listed in Table 1. It seems that the gradient B decreases as pressure increases.

O'Reilly reported that relations between temperature and pressure of dielectric loss peaks did not depend on frequency when dielectric measurements for polyvinyl acetate were done isothermally as a function of pressure (ref. 20). If correlation between freezing-in rate and dielectric relaxation time could be elucidated, these pressure dependences would give us some insight into the nature of molecular motions that concern.

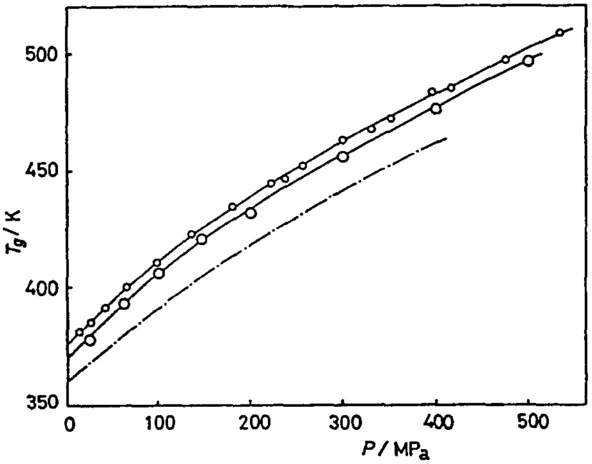

Fig. 4. Pressure dependence of Tg for anionic polystyrenes. Large circle: present data for $Mw = 1.96 \times 10^4$ frozen at 20 K/min, Small circle: DTA data for $Mw = 11 \times 10^4$ frozen at 20 K/min (ref. 21), Chain line: relation given by Oels and Rehage for $Mw = 2.04 \times 10^4$ frozen at 18 K/h (ref. 15).

TABLE 1
Constants A and B in the eqn (2) of the relation between Tg and logarithm of the freezing-in rate in K/min.

pressure / MPa	A / K	B / K decade^{-1}
0.1	365.9 ± 0.1	2.24 ± 0.10
400	472.9 ± 0.1	1.51 ± 0.21

The order parameter *z* of the glass seems to change when it is glassified under high pressure even at the same freezing-in rate. If only one *z* is enough to characterize the glass, the transition lines, $Tg(P|V)$ and $Tg(P|S)$, have to be identical when compared on the glasses prepared with the same q (ref. 3). In order to examine whether this holds or not, the present relations are compared with dilatometric data reported by Oels and Rehage (ref. 15), which are shown by triangle in Fig. 3 a) and b). Their sample was an anionic polystyrene of $Mw = 2.04 \times 10^4$ and q was 18 K/h at all pressures. For the comparison it is not necessary to take the effect of molecular weight into consideration. Their *Tg* at 0.1 MPa is lower by about 4 K than that estimated from our relation and the difference becomes larger by about 7 K at 400 MPa. To examine reliability in temperatures determined by both methods over-all *Tg-P* relations are compared in Fig. 4. It may be said that they are parallel except below 150 MPa. A *Tg* value extrapolated to 0.1 MPa from the present data by using Simon equation (ref. 22) agrees with that calculated from the relation given above. Their low *Tg* seems to be ascribed to depression due to impurities.

In order to get decisive conclusion on the issue of the number of *z* from the comparison between $Tg(P|V)$ and $Tg(P|S)$, we have to collect more exact and more reliable data on the pressure effect on *Tg*.

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