Application of a high pressure d.t.a. to study the pressure-glassification of polystyrene

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A new method to observe a pressure-glassification of polymers by using a high pressure d.t.a. is proposed. Pressure scanning, instead of the usual temperature scanning, gave a d.t.a. curve typical of the glass transition. The glass transition pressure at a constant temperature for polystyrene was determined and analysed.

(Keywords: d.t.a.; pressure scanning; glass transition pressure; glass transition temperature; polystyrene)

Differential thermal analysis is a sensitive and convenient means for studying various transition behaviours under high pressure. The high sensitivity of our high pressure d.t.a. enabled us to detect a very weak solid–solid transition of odd n-alkanes, whose heat of transition[1] was of the order of 1.4 mJ mg^{-1}. Although a heater was installed inside a d.t.a. vessel, thermal noises were relatively low. Its stability and high scanning rate made it possible to obtain d.t.a. curves[2] for the glass transition of polystyrene up to 500 MPa. During the d.t.a. run the pressure was held constant by a pressurestat, whose operational principle was based on the thermal pressure effect of a pressure transmitting liquid.

The glass transition has been recognized as a freezing-in process. Glassification is usually performed by cooling a supercooled liquid. It is well known that the stability of a glass is dependent primarily upon the 'freeing-in' rate[3,4]. Although a glass is also obtained by pressurizing the supercooled liquid at a constant temperature[5], there have been few reports of the details of this glassification.

The pressure of our d.t.a. system could be continuously increased or decreased by changing the heater temperature of the pressurestat. Through a glass transition region of polystyrene under high pressure ΔT and T signals were recorded at a constant pressurizing rate, while maintaining the d.t.a. heater at constant temperature. The ΔT signal obtained showed a discontinuity typical of the glass transition observed in a normal temperature scan of the d.t.a. This method gives information on the pressure-glassification of polymers and is useful in the study of the glass transition. This communication is a preliminary report on some of the results.

The d.t.a. cell and the high pressure system are given in Figures 1 and 2, respectively, in reference 1. In our study the heater temperature of the pressurestat was controlled by a temperature programmer. The scanning pressure range was limited to ~50 MPa. A linear rate of pressurizing or depressurizing was obtained by appropriately adjusting the heating or cooling rate of the heater. The maximum rate was ~5.7 MPa min^{-1}. A polymer sample was put into the platinum-alloy cup of the d.t.a. sensor and covered with a thin lead lid. The gap between the cup and the lid was sealed with epoxy resin. The sample weight used was ~6 mg. An alumel-chromel thermocouple was spot-welded onto the bottom of the cup, instead of soldering as in previous work[1,2]. Lead was used as a reference material. The pressure transmitting liquid was dimethylsilicone oil (10 cS). The polymer sample was an anionic polystyrene ($M_w = 1.8 \times 10^4$) purchased from Toso Corp., and was thoroughly degassed before the experiment.

Figure 1 shows a d.t.a. trace recorded at a pressure scanning rate of 3.7 MPa min^{-1} from 85 MPa at a sample temperature of 406.2 K. The sigmoidal shape of the curve indicates the glass transition. It is noted that the ΔT change is in the reverse direction to that observed on the cooling scan. The difference in the baseline is ~0.02 K. The stationary increase in the sample temperature during the pressurization was of the order of 0.005 K MPa^{-1}, following an initial transient increase. On the usual cooling curve the glass transition temperature (T_g) is customarily defined as the mid point or reflection point of the transition sigmoid. For the present case, the mid point may be defined as the glass transition pressure (P_g) which is 114.0 MPa at 406.5 K.

This sigmoid was also observed when the junction of the d.t.a. thermocouple was placed in the centre of the cylindrical sample (3 mm diameter, 4 mm high). The ΔT value observed was of the same order as that obtained by the d.t.a. cell described above. It is concluded that the ΔT discontinuity is not an artifact.

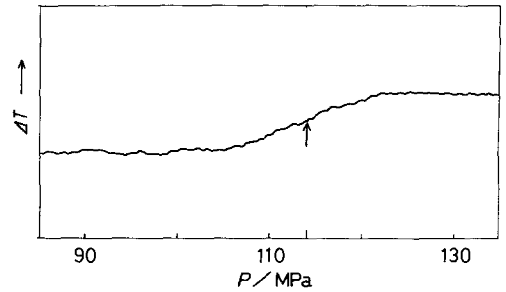

Figure 1 Pressure scanning d.t.a. curve of polystyrene ($M_w = 1.8 \times 10^4$). The scanning rate was 3.7 MPa min^{-1} from 85 MPa at 406.2 K. The arrow indicates the P_g of 114.0 MPa at 406.5 K

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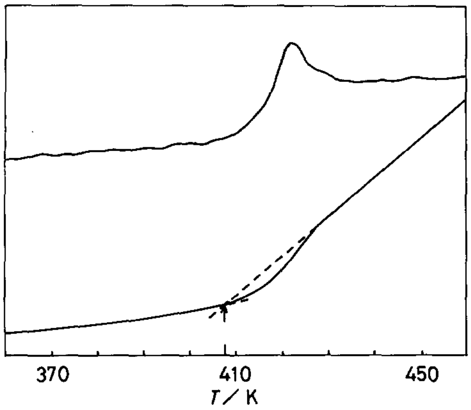

Figure 2 Temperature scanning d.t.a. curve (top) and its integrated curve (bottom) of the sample glassified by the process in *Figure 1*. The scanning rate was 20 K min^{-1} at 114.0 MPa. The direction of the ΔT curve is represented just as that for the heat flow. The arrow indicates the T_g of 407.2 K at 114.0 MPa

The validity of the P_g value was examined as follows. After pressurization up to ~135 MPa, the temperature was lowered to ~350 K, followed by depressurizing to 114.0 MPa. At that pressure the usual temperature scanning d.t.a. measurement was done at a rate of 20 K min^{-1}. The d.t.a. curve obtained is shown in *Figure 2*. A peak accompanying the glass transition is ascribed to the superheating of the glass. In order to avoid the ambiguity of the T_g determination by this effect[6], an integrated curve was calculated from the d.t.a. data and is also shown in *Figure 2*. Because of the quantitative nature of our d.t.a. measurements[7], this procedure seems to be applicable. From the intersection temperature of the liquid and the glass portions the T_g was determined as 407.2 K at 114.0 MPa. The agreement between these values and those obtained by pressure scanning is very good. It can be concluded that the ΔT discontinuity, even though small, in *Figure 1* is assigned to the glass transition at constant temperature.

Also, T_g = 408.7 K at 114.0 MPa was estimated from a relationship between T_g and pressure for polystyrene glasses vitrified at a cooling rate of 20 K min^{-1} at each pressure[8]. This slightly higher value of T_g may be ascribed to the fact that the cooling rate of 20 K min^{-1} resulted in a glass less stable than that using a pressurization rate of 3.7 MPa min^{-1}.

A problem arises in determining how strictly the sigmoidal ΔT signal could be observed using this procedure because the thermodynamic conditions in the d.t.a. cell could not be clearly defined. The temperature change of the pressure transmitting liquid was independently measured during the pressurization and was found to be similar to that observed for the sample temperature. Such a small increase of ~0.005 K MPa^{-1} indicates that the adiabatic condition does not hold during the pressurization, because the adiabatic temperature change $(\partial T/\partial P)_S$ for usual organic liquids is of the order of 0.1–0.3 K MPa^{-1}. If the constant temperature condition is held, the pressure change of the internal energy (E) consists of the heat absorbed by the compression and the work done on the system. A small change (∂P) results in $(\partial E)_T$ as follows:

$$(\partial E)_T = -(\alpha T - \kappa P)V\,\partial P \qquad (1)$$

where α is the thermal expansivity and κ the isothermal compressibility. With an assumption that the pressure change of V and the second term in equation (1) are negligible, the following equation is obtained:

$$(\partial E)_T = -\alpha V T\,\partial P \qquad (2)$$

The $(\partial E)_T$ may differ in the sample, the reference material and the pressure transmitting liquid (the surroundings). During the stationary pressure scan, steady heat flows between the sample and the surroundings and between the reference and the surroundings may occur. As one of the factors to determine the location of the baseline the heat capacity for the substances described above may have to be considered. When the polymer sample changes from liquid to glass, the baseline may change. The sign of the change in $\Delta T = T(\text{sample}) - T(\text{reference})$ coincides with that given by equation (2). This may hold if the effect of the heat capacity is small. Because the product αV in equation (2) corresponds to the pressure coefficient of the entropy surface at constant temperature, $-(\partial S/\partial P)_T$, the difference in the ΔT signal may be related to $-\Delta(\partial S/\partial P)_T$, where Δ means the difference between the glass and the liquid. Therefore, it may be reasonable to interpret the ΔT sigmoid as the glass transition at constant temperature.

Breuer and Rehage observed the glassification of polystyrene through compressibility measurements[5], and reported that the breadth of the glass transition region increased from the narrowest value of 80 MPa at 380 K. On the other hand, the breadth of our data in *Figure 1* is only ~20 MPa. Whether this difference arises from the intrinsic thermodynamic origin, that is volume or entropy, or from the operational origin have to be studied in relation to the nature of the glass transition. Another interesting subject is the effect of the rate of pressurization on the stability of a glass. These studies are now in progress.

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