Thermodynamic Studies on the Glass Transition and the Glassy State of Polymers. I. Pressure Dependence of the Glass Transition Temperature and Its Relation to Other Thermodynamic Properties of Polystyrene

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ABSTRACT: The pressure dependence of the glass transition temperature, T_g, and the coefficients of thermal expansion, α, and the compressibility, β, of polystyrene were measured. For the same sample, DSC measurement was also carried out, to obtain specific heat, C_p. From the results, it was confirmed that the relation $(\partial T_g/\partial P) \cong TV\Delta\alpha/\Delta C_p < \Delta\beta/\Delta\alpha$ was valid, in accordance with our theory based on a hole model for polymer liquids and glasses with an assumption of iso-configurational entropy at T_g. Changes of specific heats at T_g associated with intrasegmental interactions and intersegmental ones were calculated separately by the use of the theory, and $\Delta C_p^{\text{intra}} = 0.041$ and $\Delta C_p^{\text{inter}} = 0.036$ cal/gK were obtained.

KEY WORDS, Polystyrene / Glass Transition / Glassy State / Pressure Dependence / Configurational Entropy / Specific Heat / Specific Volume / Densified Glass /

It is well known that the glassy state is a thermodynamically non-equilibrium state and the glass transition is not a thermodynamic transition of the second order. However, because of this fact, it is all the more interesting to study the glassy state thermodynamically, comparing it with the crystalline or the liquid states, which is not impossible, because the glassy state can be regarded as a frozen state in a usual experimental time scale. From this point of view, many efforts have been devoted to the possibility of thermodynamic analysis of the glassy state and the glass transition temperature T_g, giving a number of interesting results. As one such result, the following relation has been discovered,[1-3]

$$\left(\frac{\partial T_g}{\partial P}\right) \cong \frac{TV\Delta\alpha}{\Delta C_p} < \frac{\Delta\beta}{\Delta\alpha} \qquad (1)$$

where T, V, and P are absolute temperature, volume, and pressure, and $\Delta\alpha$, ΔC_p, and $\Delta\beta$ are the differences in expansion coefficient, specific heat and compressibility between the liquid and glassy states at T_g respectively. Another important result is that one can obtain a glass having high density, the so-called densified glass, by glass formation under high pressure.[3-5]

On the other hand, theoretical considerations about these facts have recently been made by Nose[6] on the basis of a hole model for polymer liquids and glasses. He deduced a conclusion, in accordance with Goldstein[7] that the glass transition occurs at a state of iso-configurational entropy or energy within a substance, and derived eq 1 theoretically. Further he predicted that densified glasses should have almost the same enthalpy in the glassy state.

In the present study we will examine the above theory, particularly concerning the relationships between $(\partial T_g/\partial P)$, $TV\Delta\alpha/\Delta C_p$ and $\Delta\beta/\Delta\alpha$ experimentally, because experimental values necessary to examine eq 1 have not yet been made by the

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other research workers for the same samples, but only collected data of C_p and other values from $P-V-T$ relations which were published independently by the different authors have been used for the discussion.

EXPERIMENTAL

Sample

Commercial atactic polystyrene (Copal, Japan Olefine Co., Ltd.) was used as starting material. The material was purified by reprecipitation with acetone—n-hexane mixture. After drying for 3 day at room temperature and for 3 hr at 60°C in a vacuum oven, the obtained powder was heated in a glass tube under vacuum gradually to 200°C to produce a block sample. The intrinsic viscosity $[\eta]$ of the sample in toluene at 30°C after these treatments was 0.857 dl/g and the molecular weight was calculated as 2.7×10^5 by use[8] of $[\eta]=3.7\times10^{-4}\,M^{0.62}$. Test pieces for following experiments were provided from this block sample.

Experimental Method

P—V—T Relation. A block diagram of the pressure apparatus used is shown in Figure 1. The pressure vessel is about $60\,\mathrm{cm} \times 14\,\mathrm{cm}\phi$ in space size and is equipped with two windows
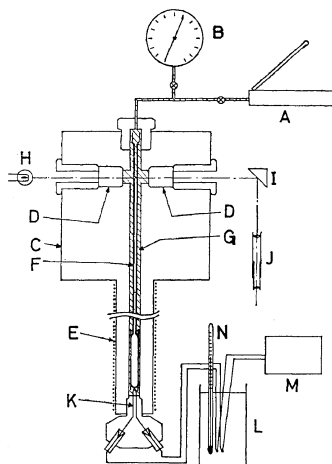

Figure 1. Apparatus for dilatometry under pressure: A, hand pump; B, 1400 kg/cm² Heise gauge; C, presure vessel; D, windows; E, heater, F, dilatometer; G, silicone oil; H, light source; I, prism; J, cathetometer; K, thermocouple; L, thermostat; M, microvoltmeter; N, thermometer.

of pyrex glasss of 17 mmϕ. An ordinary dilatometer is put in the vessel filled with silicone oil, and a change of volume, that is a change of mercury height with pressure or temperature is measured directly through these windows. In return for the advantage of direct measurement, the observable height as well as the applied pressure is restricted to a rather small range because of the limited length and strength of the glass windows. Detailed description of the pressure vessel and on the procedure of measurement will soon appear elsewhere. Care was taken to keep the vessel at uniformly constant temperature and also to measure the temperature with the same precision as pressure.

Measurements of $V-T$ relation were carried out under pressures of 150, 300, 450, and 600 kg cm^{-2}. After attaining an equilibrium in the liquid state under a given pressure, temperature was decreased at the cooling rate of 1°C/3 min, while the pressure was kept constant with a hand pump. At 30°C the pressure was released. Then densified glass was obtained. For the measurements of the $V-T$ relation under atmospheric pressure an ordinary dilatometer was used. Densities of these samples were measured by the flotation method in aqueous solutions of CaCl$_2$ at 30°C. Obtained values were averaged for 7—8 experiments excluding abnormal ones.

Compressibility of a nondensified sample was measured by the isothermal compressions at different temperatures independent of the above-described experiments.

Specific Heat. The apparatus used for specific-heat measurements was a differential scanning calorimeter manufactured by the Perkin-Elmer Corporation, Model DSC-1. The programmed temperature θ read from the instrument dial was calibrated by the melting temperatures of standard substances such as Gelium, Indium, Tin, Bismus, and Lead, each having purity in the range of 99.99—99.999%. Melting temperatures read out from recorded thermograms scattered within± 0.2 K, and θ calculated by the quadratic equation relating θ to T, which was obtained by the method of the least squares, had decrepancies within ± 0.2 K from real temperatures. Therefore the accuracy of the corrected temperature was ± 0.4 K.

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Measurements were conducted according to the reported procedures[9] with scanning interval of 85°C. Scanning speed and the sensitivity setting used were 8°C/min and 4 mcal/sec respectively. Specific heats of samples were calculated by the relationship;

$$C_p = \frac{l}{m} \times \frac{m_s C_s}{l_s} \qquad (2)$$

where C_p, l, and m are specific heat, chart-recorder displacement, and weight of the sample, and C_s, l_s, and m_s correspondingly refer to the standard material (synthetic sapphire[10]).

The observed values of specific heat of polystyrene were found to scatter within about ±2.5% for ten time experiments. Thereafter measurements were repeated three times for each sample and the obtained values were averaged.

RESULTS

Experimental values of specific volume *vs.* temperature under various pressures are shown in Figure 2 by solid circles and lines. For the reason described above, the experimental values for densified glasses were not sufficient to determine the glass transition temperatures unambiguously. However, since we have the exact value of the specific volume at 30°C under atmospheric pressure for each densified glass as shown in the figure, we can calculate the specific volume at 30°C under given pressure with the use of compressibility data. These calculated values are shown by open circles in Figure 2. It is clearly seen that these points can be connected with the experimental values for each pressure by the straight lines (dotted). The glass transition temperature was determined as the intercept of this line and the V—T line of the liquid state.

The glass transition temperatures T_g thus obtained are plotted against pressures in Figure 3 by open circles. The line segments show their possible ranges according to the extrapolation of experimental values. The glass transition temperature increases linearly with the increase of pressure. From Figure 3, $(\partial T_g/\partial P)$ was estimated to be $3.2_4 \times 10^{-2}$ K/(kg cm^{-2}).

Specific volume of the densified glass decreases with the increase of applied pressure. The magnitude of densification can be expressed by
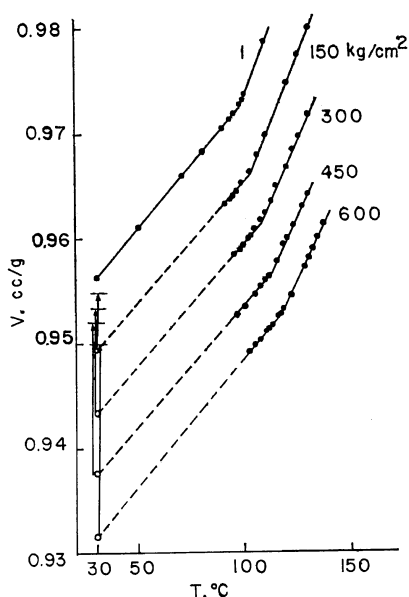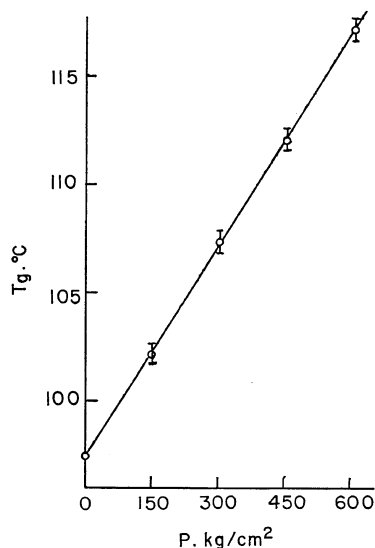

Figure 2. Specific volumes under various pressures cooled at 1°C/3 min plotted against temperature: solid lines and circles, observed; ○, calculated from specific volumes at 30°C under 1 atm; arrow, volume changes when the presure is released at 30°C.

Figure 3. T_g of polystyrene cooled at 1°C/3 min under various pressures.

the following quatities

$$\alpha' = \frac{-1}{V_s}\left(\frac{\partial V_s}{\partial T_g}\right) \qquad \beta' = \frac{-1}{V_s}\left(\frac{\partial V_s}{\partial P_g}\right) \qquad (3)$$

where V_s is the volume at a certain temperature under atmospheric pressure of the glass formed at T_g and P_g. In this study $\alpha' = 3.2_5 \times 10^{-4}\,\mathrm{K}^{-1}$ and $\beta' = 1.0_5 \times 10^{-5}\,(\mathrm{kg/cm^2})^{-1}$ were obtained at 30°C.

Figure 4 shows compressibility, β, vs. temperature curve at atmospheric pressure. From the figures, $\Delta\beta$ at 97.4°C, which is T_g under atmospheric pressure cooled at 1°C/3 min, is estimated as $\Delta\beta = 2.2_8 \times 10^{-5}\,(\mathrm{kg/cm^2})^{-1}$. From
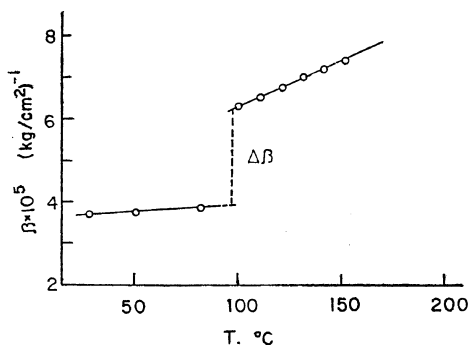

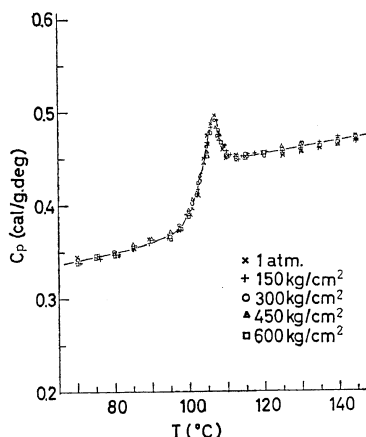**Figure 4.** Compressibilty β at atomspheric pressure plotted against temperature and $\Delta\beta$.

Figure 5. Specific heats of densified glasses of polystyrene measured with DSC using the heating rate of 8°C/min. Polystyrene cooled beforehand at 1°C/3 min under 1 atm ($\times$), 150 kg/cm² ($+$), 300 kg/cm² ($\bigcirc$), 450 kg/cm² ($\triangle$), and 600 kg/cm² ($\square$).

Figure 2 we also obtain $\Delta\alpha = 3.1_2 \times 10^{-4}\,\mathrm{K}^{-1}$ under 1 atm.

Results of specific-heat measurements are quite interesting as are shown in Figure 5. Inspite of the fact that the densified glasses were formed under different pressures and have different specific volumes as shown in Figure 2, the behavior of specific heat against temperature was almost the same, showing that densified glasses have almost the same enthalpy at least in the glass-forming conditions of this study. The difference of specific heats, ΔC_p, between the liquid and glassy states was 0.077 cal/g K at 97.4°C. This value was obtained by averaging C_p values from DSC measurements of twenty times.

DISCUSSION

First we recall some important formulae derived by Nose[6] concerning the pressure dependence of the glass transition temperature. The theory is developed from the hole theory for polymer liquids and glasses.

Defining the configurational entropy S^c as the entropy which is frozen in the glassy state, we have

$$\left(\frac{\partial T_g}{\partial P}\right) = \frac{TV\Delta\alpha}{\Delta C_p - T(\partial S^c/\partial T)_{T_g}} \qquad (4)$$

where the symbol $(\partial X/\partial Y)_{T_g}$ denotes the change in X with Y along T_g. We also have another expression for the pressure dependence of the glass transition temperature as

$$\left(\frac{\partial T_g}{\partial P}\right) = \frac{\Delta\beta}{\Delta\alpha + \alpha'} = \frac{(\Delta\beta - \beta')}{\Delta\alpha} \qquad (5)$$

where

$$\alpha' = -\tilde{V}^{-1}(\partial\tilde{V}/\partial T)_{T_g}$$

and

$$\beta' = -\tilde{V}^{-1}(\partial\tilde{V}/\partial P)_{T_g} \qquad (6)$$

In eq 6, $\tilde{V}$ is the reduced volume defined by $\tilde{V} \equiv V/V^*$ where V^* is the cell volume. From the assumption involved in the theory, α' and β' defined by eq 6 are identical with those defined by eq 3. If the iso-free volume is valid at T_g, that is, $(\partial\tilde{V}/T)_{T_g} = 0$, then we have, from eq 5,

$$(\partial T_g/\partial P) = \Delta\beta/\Delta\alpha \qquad \text{(iso-free volume)} \qquad (7)$$

If the iso-configurational entropy (iso-S^c) is satis-

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Table I. Numerical results

T_g (1°C/3 min, 1 atm)	97.4, °C
V at 97.4°C	0.9725, cc/g
$\Delta\alpha$	$3.1_2 \times 10^{-4}$, K^{-1}
$\Delta\beta$	$2.2_8 \times 10^{-5}$, (kg cm^{-2})$^{-1}$
ΔC_p	0.077, cal/g K
$\alpha' = -(\partial \ln V_s/\partial T_g)$	3.3×10^{-4}, K^{-1}
$\beta' = -(\partial \ln V_s/\partial P_g)$	$1.0_5 \times 10^{-5}$, (kg cm^{-2})$^{-1}$
$(\partial T_g/\partial P)$	3.2×10^{-2}, K/(kg cm^{-2})
$TV\Delta\alpha/\Delta C_p$	3.4×10^{-2}, K/(kg cm^{-2})
$\Delta\beta/(\Delta\alpha+\alpha')$	3.6×10^{-2}, K/(kg cm^{-2})
$(\Delta\beta-\beta')/\Delta\alpha$	3.9×10^{-2}, K/(kg cm^{-2})
$\Delta\beta/\Delta\alpha$	7.3×10^{-2}, K/(kg cm^{-2})

factory at T_g, that is, $(\partial S^c/\partial T)_{T_g}=0$, then we obtain, from eq 4 and 5,

$$\left(\frac{\partial T_g}{\partial P}\right) = \frac{TV\Delta\alpha}{\Delta C_p} = \frac{\Delta\beta}{\Delta\alpha+\alpha'} = \frac{\Delta\beta-\beta'}{\Delta\alpha} \quad (8)$$

The eq 8 gives quantitative relations between $(\partial T_g/\partial P)$ and the magnitude of densification. It must be noticed here that the iso-S^c is equivalent to iso-configurational energy under low pressure.[6]

Results obtained in the present work are summarized in Table I. From these results we can conclude within experimental precision that

$$\left(\frac{\partial T_g}{\partial P}\right) \cong \frac{TV\Delta\alpha}{\Delta C_p} \cong \frac{\Delta\beta}{\Delta\alpha+\alpha'} \cong \frac{\Delta\beta-\beta'}{\Delta\alpha} < \frac{\Delta\beta}{\Delta\alpha} \quad (9)$$

These results show that not iso-free volume but iso-configurational energy or entropy is valid at T_g and is consistent with that fact, according to the theory,[6] that heats of solution of densified glasses are similar, on which we will show experimental results supporting the theory in the next paper.

According to Nose's theory, the, specific heat change at T_g arising from intersegmental interactions, $\Delta C_p{}^{\text{inter}}$ and that associated with intrasegmental ones, $\Delta C_p{}^{\text{intra}}$ are expressed by

$$\Delta C_p{}^{\text{inter}} = \frac{TV(\Delta\alpha)^2}{\Delta\beta}$$

$$\Delta C_p{}^{\text{intra}} = \Delta C_p - \frac{TV(\Delta\alpha)^2}{\Delta\beta} \quad (10)$$

Using the data shown in Table I, we obtain $\Delta C_p{}^{\text{inter}}=0.036$ cal/g K and $\Delta C_p{}^{\text{intra}}=0.041$ cal/g K, which will be also compared with the values from heat of solution in the next paper.

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