Thermodynamic Studies on the Glass Transition and the Glassy State of Polymers. III. Poly(α -methylstyrene)

Shoji ICHIHARA*, Akihiko KOMATSU**, and Toshio HATA

Department of Polymer Chemistry, Tokyo Institute of Technology, Tokyo, Japan

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ABSTRACT: For two series of glasses of poly(α -methylstyrene), the densified glasses formed under various high pressures at the ordinary cooling rates (1°C/min) and slowly cooled glasses formed at various slow rates of cooling under atmospheric pressure, heats of solution, and specific heats were measured. In the glass-forming processes, dilatometric measurements were also made. The results differ in many points from those of polystyrene reported in previous papers. For example, the glass transition temperature T_g , the specific volume V_s at 30°C, and heat of solution or the enthalpy H of the densified glass do not vary linearly with the glass-forming pressure P . Consequently $(\partial T_g / \partial P)$ and $(\partial H / \partial P)$ decrease and $\beta' = -(\partial \ln V_s / \partial P)$ increase with increase of pressure. However, the theoretical relations about $(\partial T_g / \partial P)$ derived by Nose are shown to be valid in these cases too, at least below the pressure of 450 kg/cm². The criterion of the iso-configurational entropy or energy for T_g is established only under near atmospheric pressure. For the slowly cooled glasses, the relations $\Delta H = \Delta C_p \Delta T_g$ and $\Delta V = V \Delta \alpha \Delta T_g$ are derived and confirmed. The small value of $\Delta C_p^{\text{intra}}$ calculated is discussed in comparison with the value for polystyrene, where $\Delta C_p^{\text{intra}}$ is the specific heat change at T_g associated with intra-molecular degrees of freedom.

KEY WORDS Poly(α -methylstyrene) / Glass Transition / Glassy State / Pressure Dependence / Configurational Entropy / Specific Heat / Enthalpy / Specific Volume / Densified Glass / Annealed Glass /

In previous papers,^{1,2} we have shown for polystyrene that the glass transition temperature, T_g , of the densified glass which was formed under elevated pressure obeys the relations

$$\left(\frac{\partial T_g}{\partial P} \right) = \frac{TV\Delta\alpha}{\Delta C_p} < \frac{\Delta\beta}{\Delta\alpha}, \quad (1)$$

where $\Delta\alpha$, $\Delta\beta$, and ΔC_p are the differences of thermal expansion coefficients, compressibilities, and specific heats between the liquid and glassy states and P , V , and T are pressure, volume, and temperature respectively. The enthalpy remains constant for the glasses formed under different pressures, notwithstanding the considerable difference of T_g and specific volume. Corresponding to this fact, the behaviors of specific

heats against temperature are also the same as each other. All these facts have been explained by the concept of the iso-configurational energy or entropy at T_g as pointed out by Nose.³

On the other hand, enthalpies of the slowly cooled glasses which were formed by cooling at different rates decrease with the decrease of T_g . The decrease of the enthalpy has been shown to be equal to $\Delta C_p \times \Delta T_g$ both experimentally and theoretically.

In this paper we apply the same analysis to the glasses of poly(α -methylstyrene) with interest in the small difference of the molecular structure and consequently of inter- and intra-segmental interactions from polystyrene.

EXPERIMENTAL

Samples

Poly(α -methylstyrene) (P α MS) was prepared by anionic polymerization with sodium naphthalene

* Present address: *Plastics Research Laboratory, Mitsubishi Petrochemical Co., Yokkaichi, Mie, Japan.*

** Present address: *Showa Denko Co., Tamagawa, Ohta-ku, Tokyo, Japan.*

as a catalyst. The obtained polymer was purified by repeated reprecipitations with benzene and *n*-hexane. After sufficient drying (for 3 day under atmospheric conditions, for a week under vacuum, and for 3 day at 180°C under vacuum), the powders were heat-molded at 200–210°C to a block sample.

Two series of glasses were prepared from this block sample; the densified glasses and the slowly cooled glasses. The former were formed under the pressures of 1 atm, 150, 300, 450, and 600 kg/cm² with the cooling rate of 1°C/3 min and the latter were glassified with the cooling rates of 1°C per 3 min, 1, 3, and 10 hr, and 1 day under atmospheric pressure.

Measurements

In the process of glass-formation, the dilatometric measurements were done at the same time. Densities, heats of solution in benzene at 30°C and specific heats were measured for each glass. The methods and apparatuses were the same as in previous papers. In this study DSC measurements were made under the conditions of scanning speed 16°C/min, sensitivity 4 mcal/sec, and scanning interval 110°C. The standard deviations of the measured values were 0.0002 cc/g for specific volume, 0.6% for heat of solution, and 0.005 cal g⁻¹ K⁻¹ or 1.1% for specific heat.

RESULTS

Results from P – V – T relations

In Figure 1 the glass transition temperatures T_g of slowly cooled glasses are shown against

Figure 1. T_g of PαMS under 1 atm plotted against $\ln(\text{cooling rate in } ^\circ\text{C/hr})$.

Figure 2. T_g of PαMS cooled at 1°C/3 min plotted against applied pressure: ○, observed; ▲, calculated by eq 2; ■, calculated by eq 4.

Figure 3. $(\partial T_g / \partial P)$ plotted against mean values of pressure.

Figure 4. Specific volumes V of PαMS at 30°C plotted against T_g in the processes of glass-formation; ●, slowly cooled glass; ○, densified glass; ⊙, glass cooled at 1°C/3 min under 1 atm.

logarithmic cooling rates and in Figure 2 those of densified glasses are shown against pressures. In the present study for P α MS, the relation between T_g and pressure is not linear, being different from that for polystyrene (PS). Solid triangles and squares in Figure 2 are the calculated values in the next section. Figure 3 shows $(\partial T_g/\partial P)$ against pressure. Here $(\partial T_g/\partial P)$ was approximated by $\Delta T_g/\Delta P = [T_g(P_2) - T_g(P_1)]/(P_2 - P_1)$, and the pressure was the mean value, $(P_1 + P_2)/2$.

Figure 4 shows the relations of T_g to the specific volumes at 30°C of the densified glasses and slowly cooled glasses. In the case of PS, those of the densified glasses showed the linear relation up to 600 kg/cm² but here did not do so. The decrease of the specific volumes of the slowly cooled glasses is nearly equal to $V\Delta\alpha T_g$ (see the next section).

In Figure 5a the specific volumes of the densified glass and in Figure 5b $\beta' = -(\partial \ln V/\partial P) \cong -(\Delta \ln V/\Delta P)$ are shown against the glass-forming pressures. In the latter figure, the pressure of the abscissa is taken as a mean value of the pressures, between which β' is estimated.

Figure 5a. Specific volumes of densified glasses at 30°C plotted against the pressure applied in the processes of glass-formation.

Figure 5b. Pressure dependence of β' .

Results of thermal measurements

The heats of solution, Q , at 30°C of two series of glasses vs. T_g are shown in Figure 6. Here again the constancy of Q of the densified glasses is not found. In Figure 7a Q and in Figure 7b $(\partial H/\partial P) \cong (\Delta H/\Delta P)$ are shown against the glass-forming pressures. In the case of PS $(\partial H/\partial P)$ is zero up to 600 kg/cm², corresponding to the

Figure 6. Heats of solution Q of P α MS to benzene at 30°C plotted against T_g in the processes of glass-formation. ●, slowly cooled glass; ○, glass cooled at 1°C/3 min under 1 atm.

Figure 7a. Heats of solution of densified P α MS to benzene at 30°C plotted against the pressure applied in the processes of glass-formation.

Figure 7b. Pressure dependence of $(\partial H/\partial P)$.

Figure 8. Specific volumes of densified glasses plotted against heats of solution to benzene at 30°C: ●, slowly cooled glass; ○, densified glass; ⊙, glass cooled at 1°C/3 min under 1 atm.

constancy of the heat of solution. Figure 8 illustrates the relations of the heats of solution to the specific volumes at 30°C for both series of glasses.

Specific heats, C_p , vs. temperature are shown in Figure 9 for the slowly cooled glasses and in Figure 10 for the densified glasses. The slower the rate of cooling, the higher is the peak of specific heat. This behavior is quite similar to that found in PS² and the isothermally annealed glasses⁴ of PS. On the other hand,

Figure 9. Specific heats of slowly cooled PαMS measured with DSC using the heating rate of 16°C/min, cooled beforehand under 1 atm at 1°C/3 min, (x), 1°C/hr (○), 1°C/3 hr (+), 1°C/10 hr (△) and 1°C/day (▽).

Figure 10. Specific heats of densified PαMS measured with DSC using the heating rate of 16°C/min, cooled beforehand at 1°C/3 min under 1 atm (x), 150 kg/cm² (○), 300 kg/cm² (△), 450 kg/cm² (+), 600 kg/cm² (▽).

the behavior of the densified glasses of PαMS differs considerably from that of PS, namely, in the present case of PαMS, the peak of C_p becomes smaller and the transition temperature becomes lower with the increasing of glass-forming pressure, whereas in the case of PS, C_p vs. temperature relation for densified glasses is almost the same despite the difference of the pressure and the specific volume.

Numerical results

Numerical results are summarized in Table I. The values of T_g , V at T_g , ΔC_p , $\Delta\alpha$ and $\Delta\beta$ are those under atmospheric pressure. The value of $(\Delta T_g/\Delta P)$ is the mean value between 1 atm and 150 kg/cm². To obtain ΔC_p , we measured the specific heats of quenched PαMS twenty times with DSC and averaged.

Table I. Numerical results

T_g (1 atm, 1°C/3 min)	166.5	°C
V at T_g	0.9584	cc/g
$\Delta\alpha$	3.98×10^{-4}	K ⁻¹
ΔC_p	0.076	cal/g K
$\Delta\beta$	2.06×10^{-5}	(kg/cm ²) ⁻¹
$TV\alpha/\Delta C_p$	0.052	K/(kg/cm ²)
$\Delta\beta/\Delta\alpha$	0.052	K/(kg/cm ²)
$(\partial T_g/\partial P)^a$	0.039	K/(kg/cm ²)

^a Mean value between 1–150 (kg/cm²). The other values are those under 1 atm.

DISCUSSION

The fact that the specific volumes at 30°C were not equal to each other, *i.e.*, β' was not

zero, show the invalidity of the concept of the iso-free volume at T_g .

The pressure dependence of T_g is expressed in terms of β' by³

$$\left(\frac{\partial T_g}{\partial P}\right) = \frac{\Delta\beta - \beta'}{\Delta\alpha} \quad (2)$$

The values of T_g calculated by this equation are plotted in Figure 2 with triangles. In the calculation the value of β' is taken from Figure 5b, and $\Delta\alpha$ and $\Delta\beta$ used are those under atmospheric pressure. The use of $\Delta\alpha$ and $\Delta\beta$ under atmospheric pressure caused no large error. The calculated values agree well with the experimental ones except that for 600 kg/cm².

If the criterion of iso-configurational entropy (iso- S^c) or energy (iso- U^c) is valid for T_g under elevated pressure, the heats of solution of the densified glasses should be constant and $(\partial H/\partial P)$ should be zero, which is almost equal to $(\partial U^c/\partial P)$ when H is measured at the same temperature and pressure, because U^c is defined as the internal energy frozen in at T_g and remains constant in the glassy state.³ The results shown in Figures 6 and 7a show that these predictions are not established. However, if we extrapolate the values $(\partial H/\partial P)$ to $P=0$, they become nearly zero, that is, $(-0.5 \pm 1.7) \times 10^{-3}$ cal/g(kg/cm²). Thus, it can be said that, below the pressure of 25–50 kg/cm², the iso-configurational entropy may be valid within the precision of the experiments.

According to Nose,³ the relation between $(\partial T_g/\partial P)$ and U^c under low pressure is theoretically expressed as

$$\left(\frac{\partial T_g}{\partial P}\right) = \frac{TV\Delta\alpha}{\Delta C_p - \left(\frac{\partial U^c}{\partial T_g}\right)} \quad (3)$$

The alternative expression of the above equation is

$$\left(\frac{\partial T_g}{\partial P}\right) = \frac{TV\Delta\alpha + \left(\frac{\partial U^c}{\partial P}\right)}{\Delta C_p} \quad (4)$$

The values of T_g calculated by eq 4 using experimental values of $\Delta\alpha$, ΔC_p and $(\partial U^c/\partial P) \cong (\partial \Delta H/\partial P)$ from Figure 7b are plotted in Figure 2 with solid squares. The validity of eq 4 is also confirmed under the pressure range below

450 kg/cm².

The discrepancy of T_g between the experimental and the calculated values in Figure 2 is not clear in the present stage. It is difficult to believe that T_g has the maximum value against pressure, because the mobility of the segments may become smaller and smaller with the increase of pressure. If T_g determined by the dilatometry of the glass formed under 600 kg/cm² is true, there should be some reason for the abnormal decrease of the enthalpy and the specific volume of this glass. Supposing the crystallization, we can explain the decrease, but not the behavior of the specific heat. It is shown by the measurements of $[\eta]$ before and after the glassification that the possibility of degradation can be neglected. Further investigation is necessary to make clear this discrepancy.

Next, for the slowly cooled glasses, we derived the following relation for ΔH observed in Figure 6 in a previous paper and have shown its agreement with the experiments.²

$$\Delta H = \Delta C_p \Delta T_g \quad (5)$$

where ΔC_p is the difference of specific heats between the liquid and glassy states and ΔT_g is the difference of the glass transition temperatures due to the different glass-forming conditions. In the present study ΔC_p calculated by the above equation, that is to say, the observed slope in Figure 6 is 0.079 cal g⁻¹ K⁻¹ and ΔC_p from DSC measurement is 0.076 cal g⁻¹ K⁻¹. The derivation of eq 5 is based on the fact that the specific heats of different glasses are equal to each other.

Similarly, on the basis of the fact that $(\partial V/\partial T)_p$ is equal for glasses with different histories, we can derive the increase of specific volume ΔV with the increase of T_g of the slowly cooled glass as follows:

$$\begin{aligned} \Delta V &= \int_{T_{g2}}^{T_{g1}} \left(\frac{\partial V}{\partial T}\right)^l dT - \int_{T_{g2}}^{T_{g1}} \left(\frac{\partial V}{\partial T}\right)^g dT \\ &= \int_{T_{g2}}^{T_{g1}} \Delta \left(\frac{\partial V}{\partial T}\right) dT = \Delta \left(\frac{\partial V}{\partial T}\right) (T_{g1} - T_{g2}) \\ &= V \Delta \alpha \Delta T_g \end{aligned} \quad (6)$$

where the superscripts l and g refer to the liquid and glassy states respectively. The cal-

culated value of $\Delta\alpha$ with this equation and Figure 4 is $3.92 \times 10^{-4} \text{ K}^{-1}$ and the observed one is 3.98×10^{-4} .

The fact that the heats of solution of the densified glasses decrease with the decrease of specific volumes (Figure 8) may indicated that the decrease of intersegmental energy due to the contraction of volume is not compensated by the increase of the intrasegmental energy due to the high freezing temperature. As is discussed in the preceding paper, the difference of the specific heats due to the intrasegmental interactions between the liquid and glassy states, $\Delta C_p^{\text{intra}}$, can be calculated by²

$$\begin{aligned} \Delta C_p^{\text{intra}} &= \left(\frac{U_1^c - U_2^c}{T_{g1} - T_{g2}} \right)_{V_1=V_2} \\ &\cong \left(\frac{H_1 - H_2}{T_{g1} - T_{g2}} \right)_{V_1=V_2} \end{aligned} \quad (7)$$

at

$$T = \frac{T_{g1} + T_{g2}}{2}$$

where the subscripts 1 and 2 refer to the glasses of different histories having the same volume $V_1 = V_2$.

The value of $\Delta C_p^{\text{intra}}$ of P α MS calculated according to eq 7 is $0.007 \pm 0.01 \text{ cal g}^{-1} \text{ K}^{-1}$ which is 9 ± 13 percent of ΔC_p . In the case of PS, $\Delta C_p^{\text{intra}}$ is about 55 percent of ΔC_p . This difference between PS and P α MS may be caused by the methyl side group in P α MS.

Finally we calculated the energy difference E between *trans* and *gauche* positions with the use of the most simple isomer model such as expressed by⁵

$$\frac{\Delta C_p^{\text{intra}}}{R} = \left(\frac{E}{RT} \right)^2 \frac{2 \exp(-E/RT)}{[1 + 2 \exp(-E/RT)]^2} \quad (8)$$

Using $\Delta C_p^{\text{intra}} = 0.007 \text{ cal g}^{-1} \text{ K}^{-1} = 0.41 \text{ cal/K}$ (mole of C-C bond), we obtained two solutions of eq 8, i.e., $E = 0.81 \text{ kcal/mol}$ or $E = 5.1 \text{ kcal/mol}$. Though there is insufficient reason to choose one from the other, the value of 0.81 kcal/mol appears suitable if we compare it with the value of 2.2 kcal/mol for PS obtained in a previous paper and in view of the above discussion.

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