Volume and Enthalpy Relaxation in Polystyrene

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ABSTRACT: A study was carried out on the effects of thermal aging on specific volume V and specific enthalpy H of polystyrene below the glass transition temperature. The dependence of V and H on annealing time was similar. No significant effect of the distribution of molecular weight on the relaxation behavior was found. The behavior of V and H reaching a maximum after a double-step temperature-jump was also investigated. The time for the maximum V and H varied in proportion to the period of pre-annealing. The time for the maximum volume was slightly longer than that for the maximum enthalpy. These facts indicate that the dependence of V and H on the order parameters specifying the glassy state are similar but not exactly the same. From the enthalpy and volume relaxation curves, the enthalpy required for creating free volumes in polystyrene was calculated to be 2.0 kJ cm^{-3}. The behavior of the volume relaxation was discussed by assuming a wide distribution of relaxation time.
    KEY WORDS   Volume Relaxation / Enthalpy Relaxation / Polystyrene /
    Glass Transition / Temperature Jump / Memory Effect /

When an amorphous substance is quenched from a temperature above the glass transition temperature T_g to a temperature several degrees below T_g, extensive thermodynamic quantities such as volume and enthalpy gradually change.[1,2] Although the volume relaxation has been studied by many authors,[3-10] enthalpy relaxation,[10-13] especially the difference between volume and enthalpy relaxations, has not as yet been investigated thoroughly. The observed features of volume relaxation are summarized as follows[1-10]:

(1) The specific volume V changes in proportion to the logarithm of annealing time t.
(2) The volume relaxation time depends on the internal structure of the glass. Consequently, the volume relaxation is nonlinear in the sense that the shape of a relaxation curve depends on the volume at $t=0$.[1,2,5,10]
(3) The specific volume *vs.* time curve following a double-step temperature-jump shows a maximum.[6,9]

Calorimetric studies revealed that the first feature also appears in the enthalpy relaxation.[10] However, there are no reported studies as to whether the second and third features can be seen in the en-thalpy relaxation. In this paper, we compare the volume and enthalpy relaxations of a polystyrene sample measured under the same conditions, with special reference to the third feature.

Most of the studies on volume and enthalpy relaxation were carried out on polymer samples with a broad distribution of molecular weight, except for that of Endo *et al.*[8] who investigated the volume relaxation of narrow distribution poly(α-methylstyrene). It was shown that the molecular weight distribution affects slightly the behavior of volume relaxation. In the present study, we also measured volume and enthalpy relaxation, using narrow distribution polystyrenes.

EXPERIMENTAL

Samples.   Two polystyrene samples purchased from Pressure Chemicals Co. were used after being dried under a vacuum of 1 Pa at 60°C for 48 h. These samples had molecular weights of 4000 and 3.9×10^5, and were designated as PS(L) and PS(H), respectively. Their weight to number average molecular weight ratios were less than 1.1.

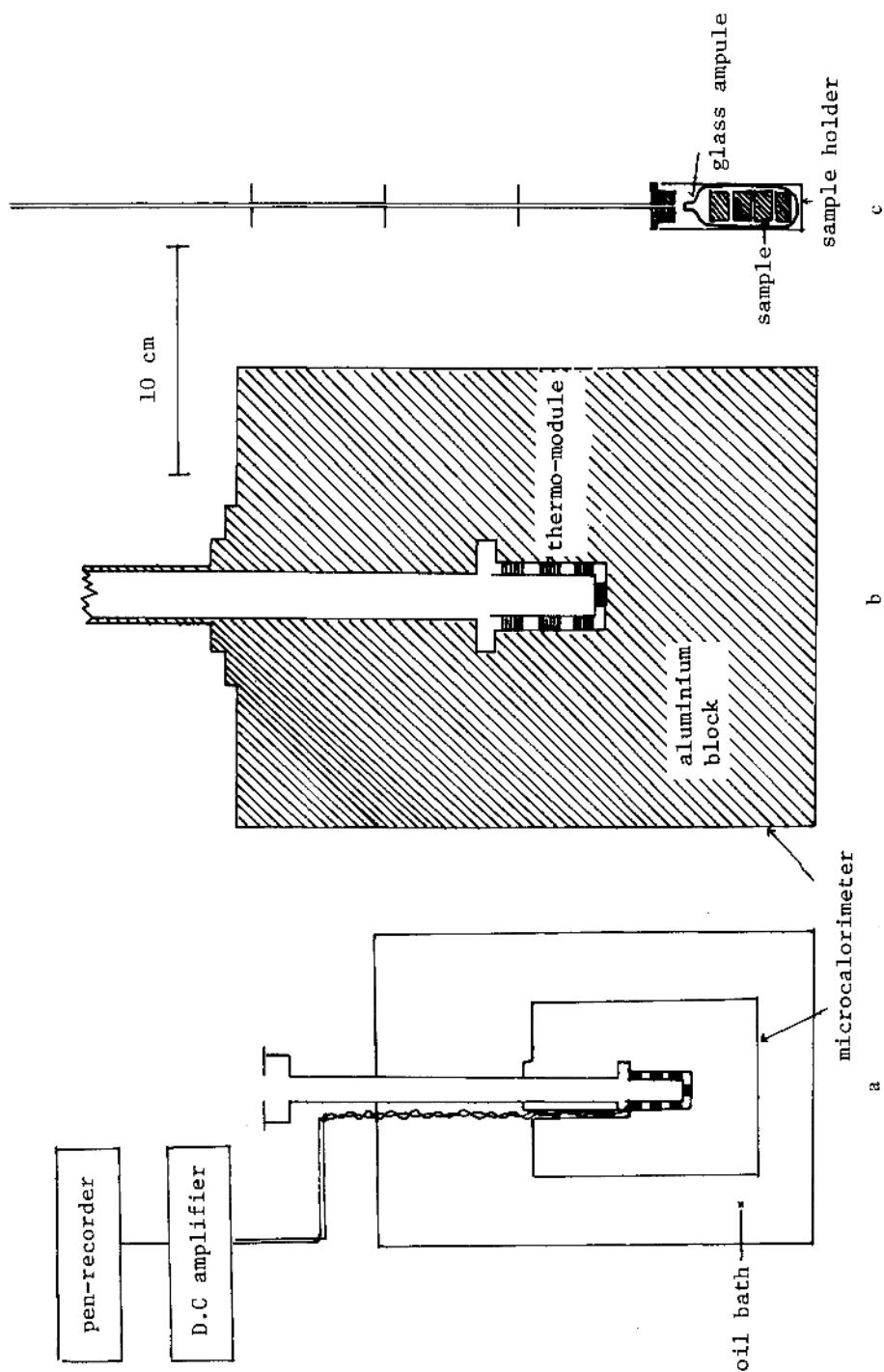For dilatometry, the dried PS(H) and PS(L) were

Figure 1. a: Schematic diagram of the micro-calorimeter of iso-thermal wall type.
b: Cross section of the calorimeter.
c: Sample holder for the measurement of enthalpy relaxation.

compression molded into films of about 1 mm thick at 180 and 100°C, respectively. For the measurement of enthalpy relaxation, PS(H) was molded also at 180°C into disks of 1 cm wide and 1 cm thick.

Methods   Enthalpy was measured with a microcalorimeter of the isothermal-wall type designed by us and constructed by Tokyo Riko Co. (Model SCC-1). A cross-sectional view of the calorimeter is shown in Figure 1. About 3.9 g of PS(H) were used for the calorimetry after being dried under a vacuum of 10^{-1} Pa for 20 h and sealed in a glass ampule with helium. The ampule was set in a sample holder, as shown in Figure 1c. The sample holder was then inserted in the calorimeter (Figure 1b). The rate of heat absorption or evolution, dq/dt, from the sample, being proportional to the temperature difference ΔT between the sample holder and the aluminium block (Figure 1b), could be determined by means of ΔT. In this calorimeter, ΔT was measured by 13 thermo-modules (Melcor Co.) connected in series. The sensitivity of these thermo-modules was about 17 mV K^{-1}. The electric signal from the modules was amplified by a DC amplifier (Ohkura Seisakusho, Model AM-1001) and traced on a pen-recorder. The proportionality constant between dq/dt and ΔT was determined to be about 6.7×10^{-2} Js^{-1} K^{-1} by measuring the heat from a resistance to which a definite current was applied for a definite period of time. The temperature of the oil bath (Figure 1a) was controlled within $5 \times$·10^{-4} K. Thus heat evolution or absorption could be measured within a precision of about 1×10^{-5} Js^{-1}.

Volume relaxation was measured with a conventional dilatometer, whose details have been described elsewhere.[10] The temperature of the oil bath for this experiment was regulated within 0.01 K.

Both volume and enthalpy measurements were performed as follows. In a single-step temperature-jump (T-jump) experiment, the dilatometer or the sample holder of the calorimeter was kept at a temperature T_i above the T_g for ten minutes and then transferred quickly into the dilatometry oil-bath or the calorimeter thermostated at a temperature T_a to commence the measurement as a function of elapsed time t. This procedure allowed the temperature of the sample to change step-wise from T_i to T_a within a period of the time needed for heat conduction. The time constant for the heat conduction was estimated to be 13 and 45 s for the dilatometers with PS(H) and PS(L), respectively. The time constant in the enthalpy measurement was 200 s. In a two-step T-jump experiment, the specimen was first brought from $T_i(>T_g)$ to a temperature T_{a1} using the same procedure as described above, and kept at T_{a1} for a prescribed period of time x. It was then transferred to another bath or the calorimeter kept at a temperature T_{a2}. Measurement of volume or enthalpy was made as a function of elapsed time t following the second T-jump. Usually, these annealing temperatures were
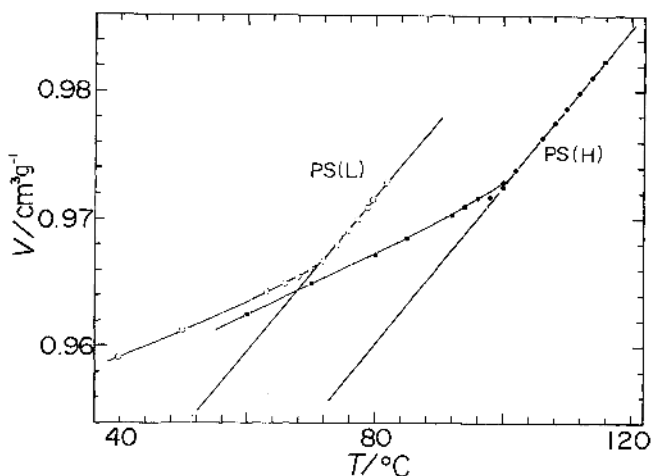

Figure 2.   Temperature dependence of the specific volume of PS(H) (●) and that of PS(L) (○) measured at the heating rate of 0.2°C min^{-1}

K. ADACHI and T. KOTAKA

chosen as

$$T_i > T_g > T_{a2} > T_{a1} \; .$$

RESULTS

The temperature dependence of the specific volumes of PS(H) and PS(L) measured by raising the temperature at a heating rate of *ca.* 0.2°C min⁻¹ is shown in Figure 2. A clear change in the slope of the curve is seen, indicating that T_g at this heating rate is 100.6 for PS(H) and 71.4°C for PS(L). The volume relaxation curves of PS(L) following T-jumps from 90°C to various temperatures below T_g are shown in Figure 3, in which only the relative change in the specific volume ΔV is shown as a function of log t in order to compare all the data in one diagram. Figure 4 shows the volume changes in

PS(L)

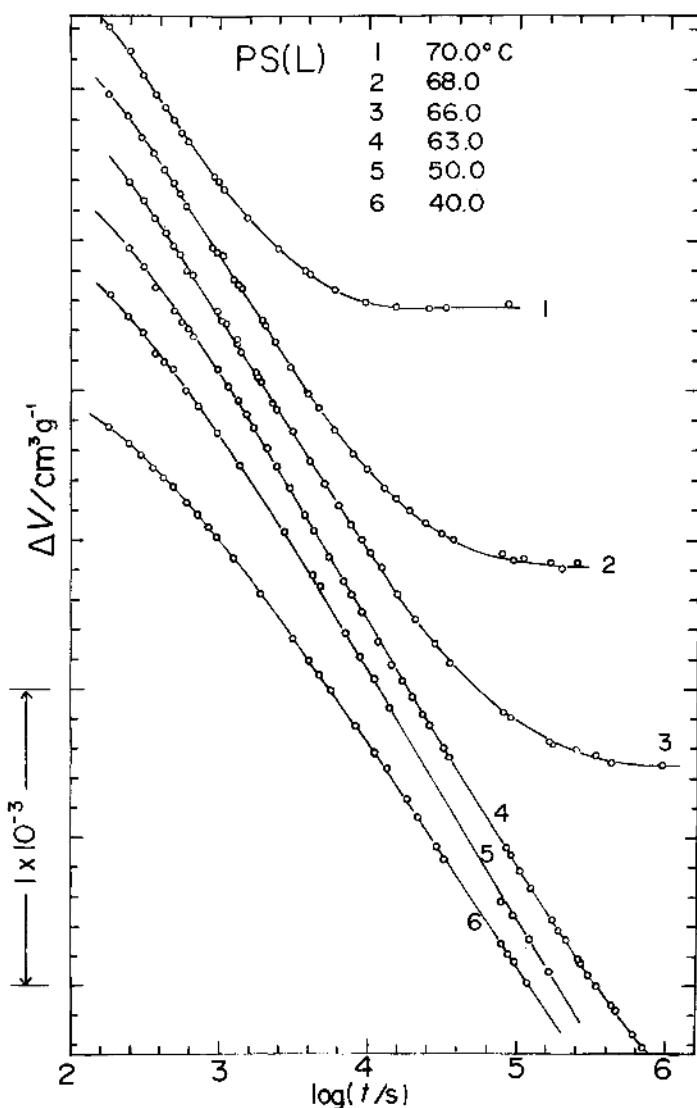|		
1	70.0° C
2	68.0
3	66.0
4	63.0
5	50.0
6	40.0

Figure 3. Volume relaxation curves of PS(L) after temperature jumps from 90°C to various temperatures T_a. The absolute values of the specific volumes at 300 s are as follows: curve 1, 0.9661; curve 2, 0.9655; curve 3, 0.9650; curve 4, 0.9643; curve 5, 0.9610; curve 6, 0.9586 (in cm³ g⁻¹).

PS(H) following T-jumps from 120°C to various temperatures. When the annealing temperature T_a was close to T_g, the equilibrium volume was attained within an annealing period of 10^6 s, as can be seen from curves 1, 2, and 3. Before attaining

equilibrium, the volume changed linearly with log t. As can be seen from Figures 3 and 4, the curves 1, 2, and 3 are almost parallel to each other, indicating the slope, $(-dV/d \log t)$, to be almost independent of T_a. This slope, a measure of the rate of volume
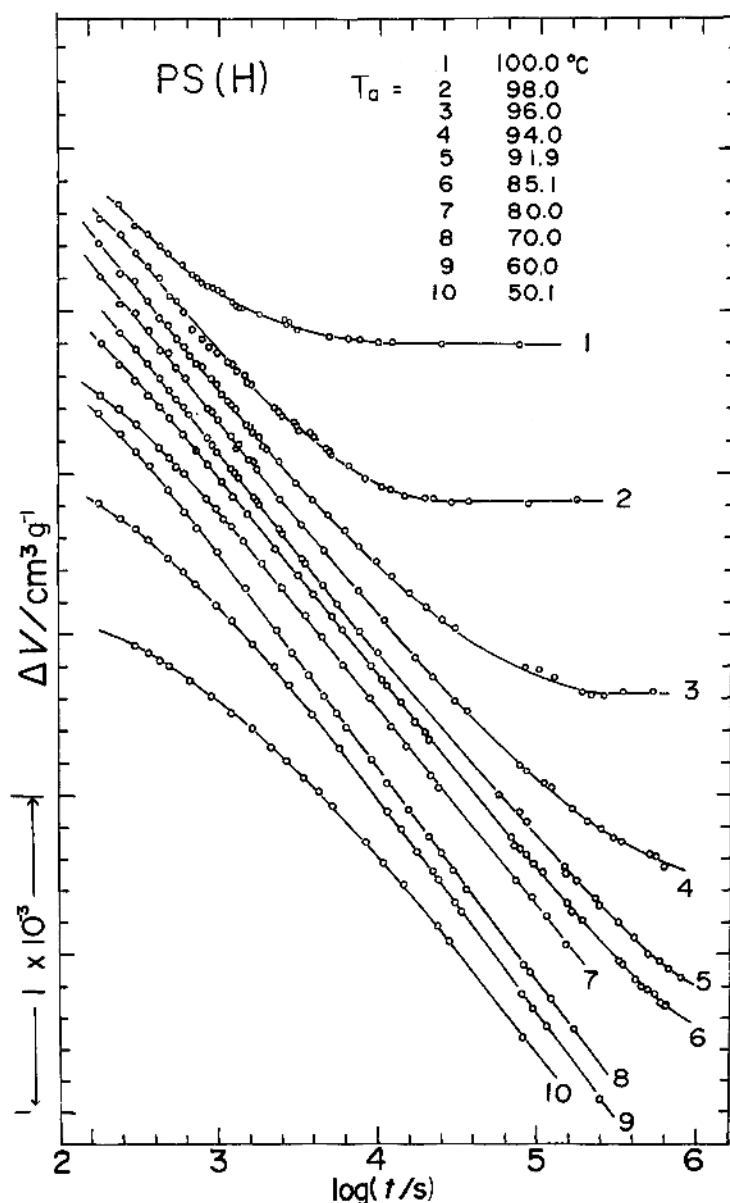
Figure 4. Volume relaxation curves of PS(H) after temperature jumps from 120°C to various temperatures T_a. The absolute values of the specific volume at 300 s are as follows: curve 1, 0.9728; curve 2, 0.9717; curve 3, 0.9716; curve 4, 0.9710; curve 5, 0.9704; curve 6, 0.9685; curve 7, 0.9672; curve 8, 0.9649; curve 9, 0.9625; curve 10, 0.9613 (in $cm^3 g^{-1}$).

relaxation, decreased slightly with increasing molecular weight, as illustrated in Figure 5. However, the molecular weight dependence of the volume relaxation is not as strong as the usual viscoelastic properties. It can be also recognized that the curves shown in Figures 3 and 4 resemble those for broad distribution polystyrenes reported by several authors.[4,5,9] No significant difference was found between the relaxation curves of broad and narrow distribution polystyrenes.

The enthalpy relaxation curves for PS(H) following the T-jumps from 120°C to 96 and 90°C are shown in Figures 6(a) and 6(b), respectively. Note that the ordinates of these figures refer to the rate of heat evolution $-\dot{H}(=-dH/dt)$, instead of the enthalpy itself. For comparison, the rate of volume contraction $-\dot{V}$ at 96°C was calculated from the volume relaxation curve (curve 3 in Figure 4), and is plotted in Figure 6(a). It can be seen that the change in $\log(-\dot{H})$ is almost parallel to that in $\log(-\dot{V})$, indicating that the time dependence of volume and enthalpy relaxation is approximately the same.

Figures 7 and 8 show the time changes in the specific volume of PS(L) and PS(H), respectively, following the double-step T-jumps mentioned above. The values of T_i for PS(H) and PS(L) were 90 and 120°C, respectively. The values of T_{a1}, T_{a2}, and x are indicated in the figure. These figures show an unusual phenomenon in which the specific volume first increases, passes through a maximum,
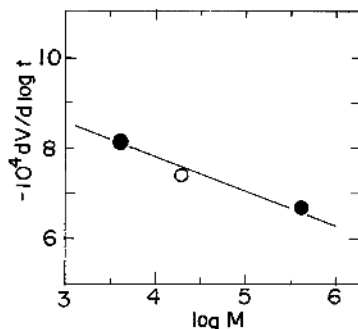

Figure 5. Molecular weight dependence of the slope of the volume relaxation curve in polystyrene. ●, present data; ○, by Kovacs.[5]
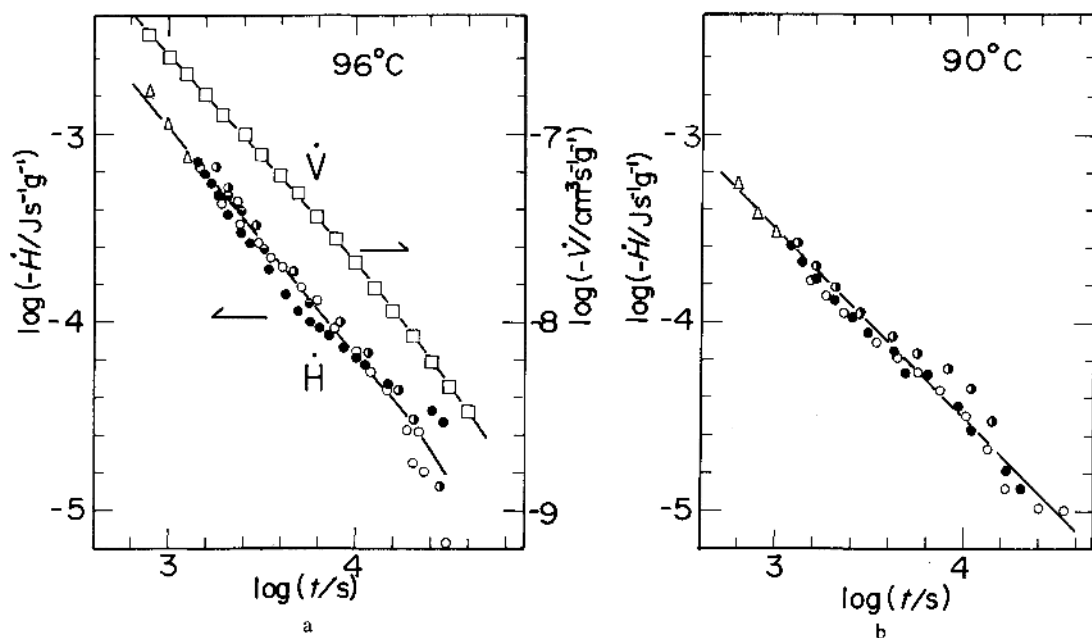

Figure 6. a) Time dependence of the rate of the enthalpy change $\dot{H}=dH/dt$ and that of the volume change $\dot{V}=dV/dt$ for PS(H) at 96°C. Different keys for $\dot{H}$ represent the data in the different series of measurements repeated under the same condition.
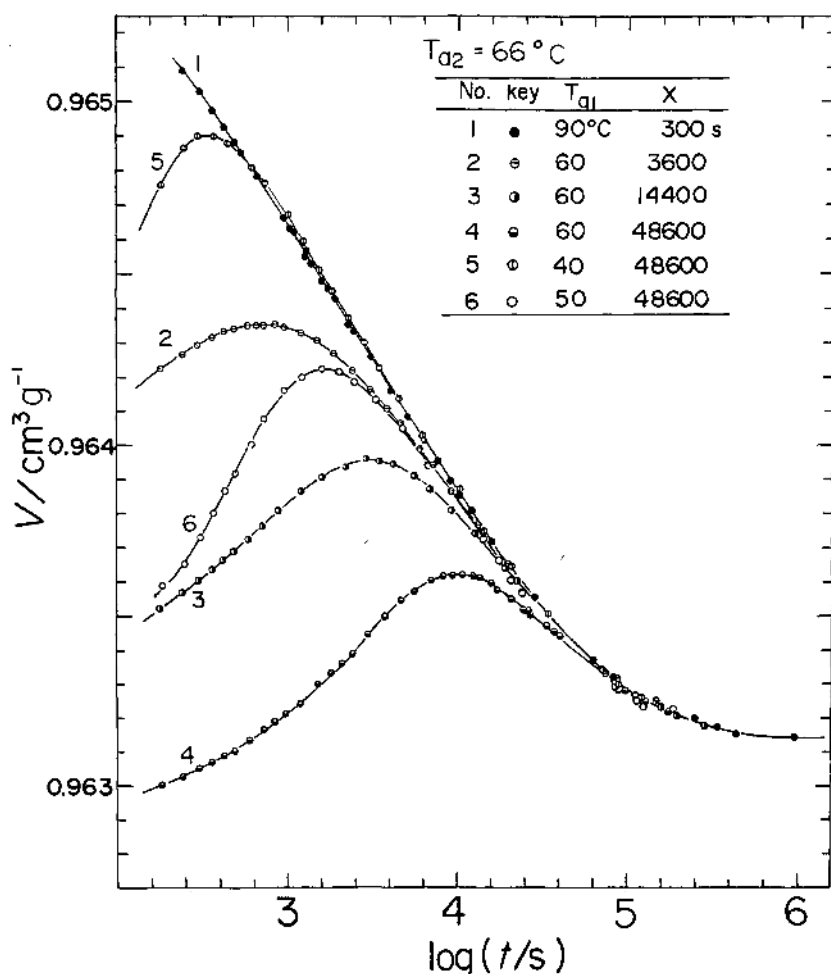b) The enthalpy change for PS(H) at 90°C.

Figure 7. Volume change in PS(L) after double temperature jumps. T_{a1}, T_{a2}, and x (see text) are given in the figure.

and then decreases to an equilibrium value. This phenomenon was first found by Kovacs and called the memory effect.[6] This effect was found in the present study and is similar to that observed by Hozumi on a broad distribution polystyrene sample.[9] Therefore, the volume relaxation due to the memory effect is independent of molecular weight distribution. The memory effect in the enthalpy relaxation of PS(H) is shown in Figure 9, in which the ordinate indicates the rate of heat evolution $-\dot{H}(= -dH/dt)$, instead of the enthalpy itself. An endothermic change occurs in the initial stage of the relaxation, but after some annealing, the change becomes exothermic. It should be noted that the time at which $-\dot{H}$ becomes zero corresponds to the

time at which the system reaches maximum enthalpy.

DISCUSSION

Comparison of Volume and Enthalpy Relaxation

As can be seen from Figure 6(a), the double logarithmic $-\dot{H}$ and $-\dot{V}$ vs. t curves for PS(H) subjected to the same T-jump are almost parallel and linear in the range of log t from 3.0 to 4.3. For t larger than $10^{4.3}$ s, both H and V approach equilibrium and hence deviate from the linear relation. In the linear range, the slope of the log $(-\dot{V})$ or log $(-\dot{H})$ vs. log t curve is approximately equal to -1. Therefore, both $\dot{V}$ and $\dot{H}$ can be represented by
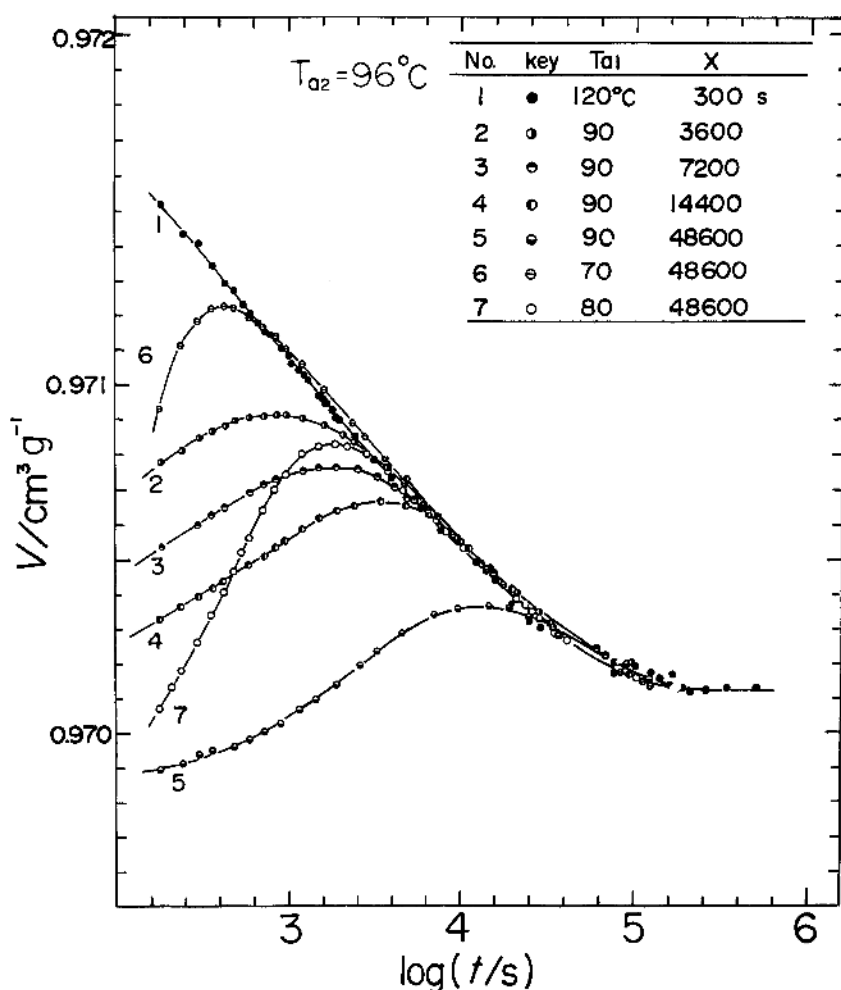
Figure 8. Volume change in PS(H) after double temperature jumps.

$$-\dot{V} = a_V/t \qquad (1)$$

$$-\dot{H} = a_H/t \qquad (2)$$

where a_V and a_H are constants. It can be shown by integrating eq 1 or 2 that V or H is proportional to $\log t$.

For a one-component system in the equilibrium state, two thermodynamic variables, normally temperature T and pressure P, are required to specify its state. However, since glass is in a nonequilibrium state, it is necessary to fix extra variables called the order parameters ξ in order to specify its state.[14-17] Thus, at constant P and T, $\dot{V}$, and $\dot{H}$ in a glassy state may be written

$$\dot{V} = \sum_i (\partial V/\partial \xi_i)_{P,T,\xi_{j\neq1}}(d\xi_i/dt) \qquad (3)$$

$$\dot{H} = \sum_i (\partial H/\partial \xi_i)_{P,T,\xi_{j\neq1}}(d\xi_i/dt) \qquad (4)$$

Since $\dot{V}$ and $\dot{H}$ depend on time as shown in Figure 6a, the ratios $(\partial V/\partial \xi_i)/(\partial H/\xi_i)$ for different ξ_i should be approximately the same. However, we note that the behavior of the volume relaxation following a two-step T-jump is slightly different in detail from the enthalpy relaxation. Figure 10 shows a plot of the time t_{max}, at which the volume or the enthalpy exhibits a maximum in a two-step T-jump test against the pre-annealing time x. It is seen that the time to reach the maximum volume is slightly longer
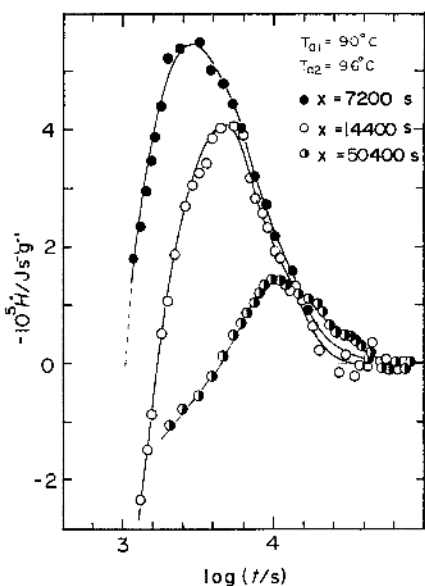
Figure 9. The rate of enthalpy change in PS(H) after double temperature jumps. $T_{a1} = 90°C$; $T_{a2} = 96°C$.
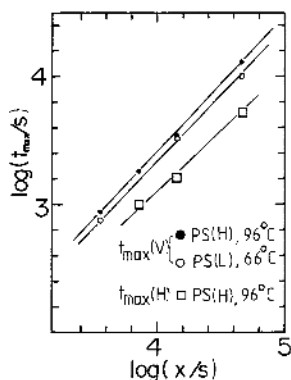

Figure 10. $\log t_{max}$ vs. $\log x$ plots in the memory behavior of volume and enthalpy.

than that for reaching the maximum enthalpy. This fact indicates that the dependence of V and H on the order parameters is similar but not exactly the same.

Rehage[15] concluded from the pressure dependence of T_g that only one order parameter is enough to describe the glassy state of polystyrene. His conclusion contradicts the memory effects shown in Figures 7, 8, and 9, which indicate that different glassy states have the same V or H. Therefore, more than two order parameters are needed to specify the state of glassy polystyrene.

The change in H relative to that in V means physically the energy for creating a unit free volume. This ratio was calculated to be $2.0 \, \mathrm{kJ \, cm^{-3}}$ from the relaxation curves at 96°C. The ratio of H to V may be regarded as a kind of internal pressure. This internal pressure is calculated to be 2.0 GPa.

Effect of Molecular Weight and Its Distribution

As pointed out above, the volume relaxation is not particularly influenced by molecular weight distribution. No significant difference in relaxation behavior was observed between narrow and broad distribution polymers. This is not surprising, since the effect of molecular weight distribution on mechanical properties in the glass transition region is usually small. As shown in Figure 5, the rate of volume relaxtion $dV/d \log t$ decreases only slightly with increasing molecular weight.

Memory Effect and Distribution of Relaxation Time

As discussed in the introduction, the volume relaxation of glassy polymers is characterized by two features: this relaxation is nonlinear in the sense that relaxation time depends on internal structure and glassy polymers exhibit a memory effect in volume relaxation following a double-step T-jump. In the present study, these features were also found in the enthalpy relaxation.

The memory effects in both volume and enthalpy relaxations may be explained qualitatively by assuming a wide distribution of relaxation time, regardless of whether the relaxation time depends on internal structure or not.

Before attempting this explanation, we should first look at the features of the memory curves. Figure 11a and 11b show schematic diagrams representing how the momory effect is influenced by the pre-annealing temperature T_{a1} and the pre-annealing time x. When x increases at constant T_{a1}, the initial volume increase, which can be approximated by a straight line, shifts parallel in the direction of increasing $\log t$, as shown in Figure 11a. The slope of this initial stage is not affected by the pre-annealing time x. On the other hand, when T_{a1} decreases at constant x, the slope of the curve increases, as shown in Figure 11b. The rate of volume change increases with a decrease in pre-annealing temperature T_{a1}.

In both cases, the volume reaches a maximum at the point where the rising portion of the curve
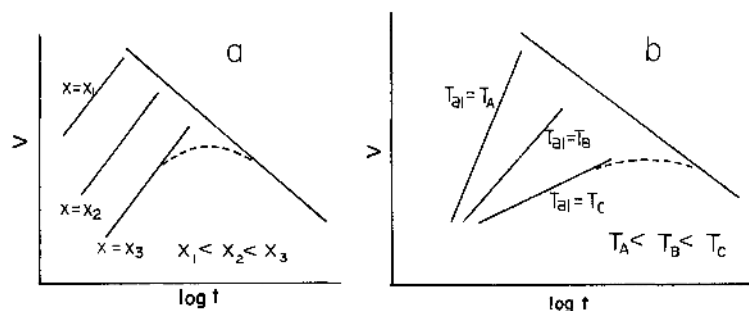
Figure 11. Effect of x and T_{a1} (see text) on the memory behavior.
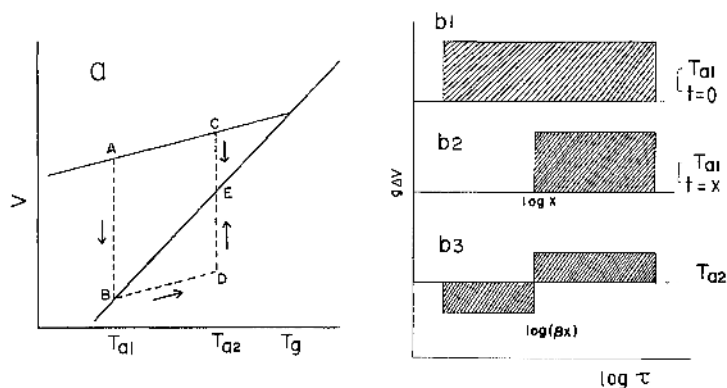

Figure 12. Schematic diagram for the explanation of memory behavior.
(a) Temperature dependence of specific volume.
(b1) Spectrum of $g\Delta V$ at T_{a1} immediately following the first temperature jump.
(b2) The spectrum after annealing for x seconds at T_{a1}.
(b3) The spectrum immediately following the second temperature jump from T_{a1} to T_{a2}. The parameter β is the factor for correction of the temperature dependence of the relaxation time.

intersects the curve following the single T-jump from a temperature above T_g to T_{a2}. After passing the maximum, the volume decrease follows the same curve as that for the single T-jump. In order to explain this behavior, we assume a box-type distribution of relaxation times shown in Figure 12(b1), where g is the number of the relaxing components in the range from $\log \tau$ to $\log \tau + \mathrm{d} \log \tau$ and ΔV is the deviation of the volume from the equilibrium value. This assumption may be justified for the following reasons based on the fact that volume decreases linearly with $\log t$ in the case of a single T-jump.

As is well known, the relaxation strength at a relxation time τ is proportional to the slope of the relaxation curve at that time τ (Alfrey's assumption). Thus, the V vs. $\log t$ curve with a constant slope gives a flat and very wide spectrum shown in

Figure 12. We now introduce three more assumptions. 1) Each component relaxes exponentially after being brought to a non-equilibrium state. Thus, the deviation in the specific volume Δv_i of the i-th component from the equilibrium value is given by

$$\Delta v_i = \Delta v_{i0} \exp(-t/\tau_i) \qquad (5)$$

where Δv_{i0} is the initial value of Δv_i. 2) The effect of each component is additive, so that deviation in the volume of a bulk sample from equilibrium is given by $\sum g_i \Delta v_i$. 3) The temperature dependence of the specific volume v_i of the i-th component is the same as that of bulk PS, as schematically shown in Figure 12a. The exponential function in eq 5 can be approximated by a step-function. Therefore, Δv_i changes suddenly from Δv_{i0} to zero at τ_i.

At the instant this system is quenched from a temperature above T_g to T_{a1}, the spectrum is assumed to have the form depicted in Figure 12(b1). The annealing at T_{a1} for x seconds gives rise to a change in the spectrum such as shown in Figure 12(b2). At this stage, the components with τ_i longer than x still remain at point A in the V vs. T diagram in Figure 12(a), while the components with τ_i shorter than x is at point B. The T-jump from T_{a1} to T_{a2} occurs next. This second T-jump shifts the point A to point C, and point B to point D. Therefore, the $g\Delta v_i$ of the components which have been at point B become negative (Figure 12(b3)), owing to the assumption 3). The volume recoveries of the negative Δv_{i0} components having relatively short relaxation times occur faster than those of the positive Δv_{i0} components with longer relaxation times. Hence, the volume initially increases with time, deviating from the equilibrium volume at T_{a2}. When the recoveries of the negative components with shorter relaxation times have been completed, the positive components start relaxing in the direction of decreasing volume. On the basis of this model, we can expect that the logarithm of the time t_{max} at which V reaches a maximum is proportional to log x and that the slope in the initial part of the relaxation curve is proportional to the volume difference between points E and D in Figure 12a. Therefore, this slope should increase with an increase in $T_{a2} - T_{a1}$. The experimental results shown schematically in Figure 11 is in agreement with this expectation.

In Figure 10, we note that log t_{max} is proportional to log x but t_{max} is about six to seven times smaller than x. This descrepancy may be due to the following two reasons: First, the relaxation time at T_{a2} is shorter than the corresponding relaxation time at T_{a1} because $T_{a2} > T_{a1}$. Second, the volume relaxation is nonlinear in the sense that the relaxation time decreases during the process of the volume increase on account of the internal structure dependence of τ_i.

Time Dependence of the Relaxation Time

So far, we have neglected the dependence of the relaxation times on the internal structure of the glass.[1,2] Consequently, the relaxation times are not constant but change with time during volume recovery. Therefore, it is important to examine how the nonlinear relaxation affects the memory effect.

It has already been shown that the dielectric relaxation time τ_D for the primary process of a poly(vinyl acetate) decreases with time during the volume relaxation below its T_g.[10] The time dependence of τ_D in the time interval in which the volume changes linearly with log t is represented by

$$\log \tau_D = \alpha \log t + B \qquad (6)$$

where α and B are constants. We note that α is positive for volume contraction and negative for volume expansion. We assume that the volume relaxation time τ_i of the i-th component in the relaxation time spectrum has a time dependence similar to that of τ_D. Thus, the time dependence of τ_i in the time interval between t_1 and t_2, where volume changes linearly with log t, is written as

$$\tau_i(t) = \tau_{i0}(t/t_1)^\alpha \qquad (t_2 > t > t_1) \qquad (7)$$

where τ_{i0} denotes the time constant at $t = t_1$ for the i-th component. Equation 7 implies that the spectrum delineated in Figure 12 shifts with time at a constant rate along the log τ axis. However, it should be noted that eq 7 is valid only for the definite time interval from t_1 to t_2, and nothing can be said about the behavior of τ_i at $t < t_1$. In the range of time shorter than t_1, the volume does not change linearly with log t as can be seen from curves 7 to 10 in Figure 4. No comment can be made about τ_i at $t = 0$, either. A very rapid T-jump from a temperature higher than the T_g to a temperature below T_g may possibly yield a glass containing a much larger free volume than that ordinary glass. Such "microporous glass" may have $\tau_{i0}(=t_1)$ shorter than that for glass quenched at a normal rate. Therefore, $\tau_{i0} = t_1$ may depend on the condition of T-jump. Thus, the rate of volume change for the i-th component is given by

$$d\Delta v_i/dt = -\Delta v_i/\tau_i(t) \qquad (8)$$

Integration of this equation gives the time dependence of v_i in the form

$$\Delta v_i(t) = c_i \exp[-A_i t^{1-\alpha}/(1-\alpha)] \quad (\alpha \neq 1) \qquad (9)$$

$$\Delta v_i(t) = c_i t^{-A_i} \qquad (\alpha = 1) \qquad (9')$$

where c_i and A_i are constants.

We examine the difference between $V(t)$ having the time dependence characterized by eq 7, 8, and 9 and $V'(t)$ having constant relaxation times. We assume that the distribution of the number of

components having relaxation time τ_i is the same in both volumes. Because $\alpha = 0$ in the case of constant relaxation time, $V'(t)$ is written

$$V'(t) = V_0(T) + \sum_i g_i c_i \exp(-A_i t) \quad (10)$$

where $V_0(T)$ denotes the equilibrium volume at a temperature T and g_i denotes the number of components having relaxation time τ_{i0}. On the other hand, $V(t)$ in the case where $\alpha \neq 1$ is given by

$$V(t) = V_0(T) + \sum_i g_i c_i \exp[-A_i t^{1-\alpha}/(1-\alpha)] \quad (11)$$

Comparison of $V'(t)$ and $V(t)$ indicates that $V(t)$ plotted against $t^{1-\alpha}/(1-\alpha)$ has the same form as $V'(t)$ plotted against t. Therefore, $V'(t)$ theoretically derived without taking the time dependence of the relaxation time into account can be transformed into $V(t)$ simply by replacing t with $t^{1-\alpha}/(1-\alpha)$ in $V'(t)$. This implies that the $V'(t)$ plotted against $\log t$ is uniformly expanded or shrunk by a factor of $1-\alpha$ along the abscissa, if the time dependence of the relaxation time is taken into account. Thus, no change is caused in the qualitative feature of the memory effect by introduction of the nonlinear volume relaxation, as far as the behavior in the time interval between t_1 and t_2 is concerned, where the volume relaxes linearly with $\log t$ in a single step T-jump test.

CONCLUSIONS

1) Volume and enthalpy relaxation of glassy polystyrene are similar but not exactly the same.

2) Memory effect can be explained on the basis of a model in which the bulk volume consists of many sub-volumes, each having a different relaxation time but depending on temperature in the same manner as the volume of the bulk polymer.

3) The effect of molecular weight and its distribution on the volume relaxation is small. The rate of volume relaxation decreases slightly with increasing molecular weight.

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