

# Structural Relaxations of Glassy Polystyrene and *o*-Terphenyl Studied by Simultaneous Measurement of Enthalpy and Volume under High Pressure<sup>†</sup>

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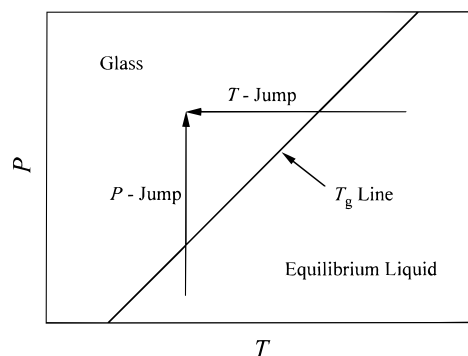
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The heat capacities, thermal expansivities, and isothermal compressibilities of polystyrene and a mixture of *o*-terphenyl (67%) and *o*-phenylphenol (33%) (abbreviated as OTP–OPP) were measured around their glass transition temperatures at atmospheric pressure and high pressure (20.8 MPa for polystyrene and 28.8 MPa for OTP–OPP). The measurements were performed simultaneously with a novel calorimeter recently developed by our group. This calorimeter works under constant pressure up to 100 MPa and in the temperature range between 80 and 380 K. The heat capacity gap  $\Delta C_p$ , thermal expansivity gap  $\Delta\alpha$ , and isothermal compressibility gap  $\Delta\kappa$  at  $T_g$  were determined precisely for both samples. The Prigogine–Defay ratio  $\Pi \equiv \Delta C_p \Delta\kappa / (TV(\Delta\alpha)^2)$  is significantly larger than unity for both samples, indicating that more than two internal parameters are necessary to specify the glassy state thermodynamically. The enthalpy and volume relaxations of the polystyrene and OTP–OPP were also measured simultaneously around  $T_g$  after the temperature- and pressure-jump processes. The relaxation paths determined in the  $\Delta H_c$ – $\Delta V_c$  plane was inconsistent with the fictive temperature concept in the structural relaxation even in the vicinity of the equilibrium state with the volume relaxing faster than the enthalpy.

## 1. Introduction

The glass transition is one of the important topics of current condensed matter physics and chemistry.<sup>1</sup> One of the powerful methods for the study of the glass transition is to measure the relaxation of some physical quantities as functions of time after a sudden change of temperature or pressure.<sup>2–9</sup> This method is called the temperature jump (TJ) or pressure jump (PJ) method, respectively. Figure 1 schematically shows the TJ and PJ processes in a pressure–temperature plane ( $p$ – $T$  plane) of a glass-forming liquid. The curve bisecting the plane represents the glass transition line defined as the locus of a constant structural relaxation time that is taken at the calorimetric time scale (ca. 1 ks). It is common that the relaxation time is long at low temperatures and high pressures, indicating that the upper-left area corresponds to the glassy state and the lower-right area the equilibrium liquid. The TJ and PJ processes are shown by the arrows. Glassy states at the same temperature and pressure can be realized by the two different paths.

Thermodynamically speaking, the enthalpy and volume measurements under pressure provide the most important information, since the Gibbs free energy, which determines the stability of a material at a given temperature and pressure, can be calculated only by these quantities. One can describe the kinetic process of a relaxing glass as a locus in a three-dimensional space spanned by the Gibbs energy, enthalpy, and volume. The simultaneous measurement is necessary because



**Figure 1.** Schematic diagram showing the temperature-jump and pressure-jump processes in a pressure–temperature plane of a glass-forming liquid. The curve bisecting the plane represents the glass transition line.

two nonequilibrium states cannot be produced precisely in the same way in two apparatuses measuring two different quantities. However, the simultaneous measurement has not been performed for any glassy materials.

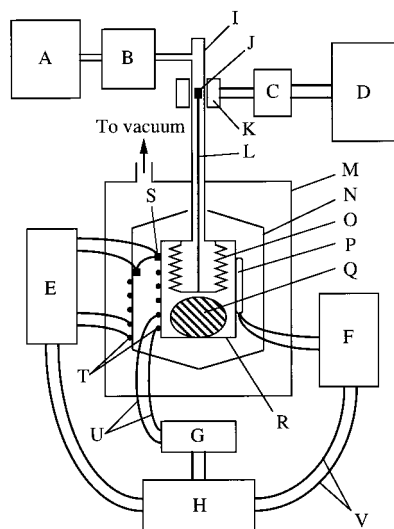
The aim of the present study is twofold. The first is to investigate the relaxation path in the enthalpy (or internal energy) versus volume plane, focusing our attention on the examination of the fictive temperature concept.<sup>10</sup> The fictive temperature is one of the traditional and important concepts for the glassy states. The fictive temperature of a glassy state is defined as the temperature at which the equilibrium liquid has the same configurational properties as those of the glassy state. If the fictive temperature concept is valid, the fictive temperatures representing different configurational properties (e.g., enthalpy and volume) of a given glass should be the same. In the relaxation at a constant temperature and pressure, therefore, the relaxation should take place along the locus followed by

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**Figure 2.** Block diagram of the calorimeter: (A) pressure generation system, (B) pressure control system, (C) volume measurement system, (D) computer, (E) adiabatic control system, (F) temperature measurement system, (G) energy supply system, (H) computer, (I) pressure transmitting tube, (J) magnet, (K) magnesensor, (L) displacement transmitting rod, (M) vacuum jacket, (N) adiabatic shield, (O) bellows, (P) Rh–Fe resistance thermometer, (Q) sample, (R) sample cell, (S) thermocouple, (T) heater wire, (U) lead wire, and (V) electric cable.

the equilibrium liquid. The simultaneous measurements give a direct experimental test of the fictive temperature theory.

The second of the aims of this study is to precisely determine the heat capacity gap  $\Delta C_p$ , thermal expansivity gap  $\Delta\alpha$ , isothermal compressibility gap  $\Delta\kappa$  at  $T_g$ , and the pressure dependence of the glass transition temperature  $dT_g/dP$ .  $\Delta C_p$ ,  $\Delta\alpha$ , and  $\Delta\kappa$  are used to evaluate the Prigogine–Defay ratio  $\Pi \equiv \Delta C_p \Delta\kappa / (TV(\Delta\alpha)^2)$ .<sup>11</sup> This quantity is related to the number of the internal parameters required to specify the glassy state thermodynamically; i.e., if  $\Pi = 1$  then one internal parameter is sufficient, but if  $\Pi > 1$  then more than one internal parameter is necessary.<sup>11,12</sup>

The samples examined in this study were atactic polystyrene and a mixture of *o*-terphenyl (67%) and *o*-phenylphenol (33%) (abbreviated as OTP–OPP hereafter). These materials were chosen, since they are typical glass-forming materials in polymer and molecular substances, respectively, and since their glass transition temperatures are suitable for the present apparatus. OPP dissolves in OTP and hinders crystallization on cooling;<sup>13</sup> pure OTP crystallizes slowly even at  $T_g$ . For polystyrene, the enthalpy and volume have been measured separately, with limited accuracies, on samples of different molecular weights.<sup>8</sup>

## 2. Experimental Section

**A. Apparatus.** All the measurements in this study were performed with a novel calorimeter recently developed in our group.<sup>14</sup> Figure 2 shows schematically the outline of the calorimeter. This calorimeter works under constant pressure up to 100 MPa and in the temperature range between 80 and 380 K. The sample is pressurized hydrostatically by using a liquid pressure transmitting medium. The sample volume is measured with a bellows-type dilatometer installed in the calorimeter. The dilatometer has two resolution modes (high and low) with different scanning ranges. In the low-resolution mode, the accuracy of the volume measurement was  $\pm 20$  ppm of the total volume. In the high-resolution mode, the volume resolution was  $\pm 0.1$  ppm of the total sample volume, which is ca. 10 times better than that of the previous best dilatometer. The calorimetric

measurement is performed with a standard adiabatic method. The resolution of the thermometer is ca. 100  $\mu$ K, and the accuracy of the sample heat capacity is ca. 0.3%.

**B. Sample Preparation.** Atactic polystyrene with a low ( $M_w = 5.97 \times 10^3$ ) and narrowly distributed ( $M_w/M_n = 1.02$ ) molecular weight was purchased from Tosoh Co. The sample (11.350 g) was dried under vacuum at 420 K for 36 h and molded in a cylindrical cup. This cup was made of poly(chlorotrifluoroethylene) (Neoflon; Daikin Kogyo Ltd.) and can deform, allowing the sample to change its volume. The mass of the cup was 3.2231 g, and the dimension was as follows: height, 47 mm; outer diameter, 19 mm; thickness, 0.3 mm. The cup filled with the sample was placed in the sample room of the cell together with 17.330 g of Fluorinert. Fluorinert (Sumitomo 3M Co. Ltd.), which is a mixture of completely fluorinated alkanes, is suitable for the pressure transmitting medium, since it dissolves neither in water nor in hydrocarbon oils. The other compartment of the cell separated from the sample room by the bellows was filled with air in the experiments at atmospheric pressure and with 1-butanol in the experiments under high pressure.

Commercial reagents of OTP (99% purity) and OPP (99% purity) were purchased from Aldrich Chemical Co., Ltd. and Wako Pure Chemical Ind., Ltd., respectively. They are mixed in crystalline states after drying in vacuo at room temperature. The composition of the sample was OTP<sub>0.66811</sub>OPP<sub>0.33189</sub>. OTP–OPP was melted, degassed, and sealed in a Neoflon cup under vacuum. The filled cup was sealed mechanically at the inlet tube. The size of the cup is as follows: height, 55 mm; outer diameter, 20 mm; thickness, 0.5 mm. 3-Methylpentane ( $T_{fus} = 100$  K,  $T_g = 77$  K) was used as the pressure transmitting medium for both the outside and the inside of the bellows in the cell.

**C. Heat Capacity and Thermal Expansivity.** Heat capacity ( $C_p$ ) and thermal expansivity ( $\alpha$ ) were measured simultaneously at 0.1 MPa (atmospheric pressure) and 20.8 MPa in the temperature range 280–380 K for polystyrene and at 0.1 and 28.8 MPa in the temperature range 185–290 K for OTP–OPP. The volume was measured in the low-resolution mode, which is suitable for the measurement of a large volume change. The temperature step of one determination of the heat capacity and thermal expansivity measurement was 2.5–3 K.

The glassy sample was prepared by cooling the liquid rapidly (2–3 K min<sup>−1</sup>) under the pressure at which the  $C_p$  and  $\alpha$  were measured. The heat capacity and thermal expansivity of the sample were calculated by using the method described elsewhere.<sup>14</sup> The absolute values of the volume of polystyrene and OTP–OPP at the reference points were determined with a pycnometer to be  $0.956 \pm 0.003$  cm<sup>3</sup> g<sup>−1</sup> (at 30 °C, 0.1 MPa) and  $1.058 \pm 0.003$  cm<sup>3</sup> g<sup>−1</sup> (at 359.8 °C, 0.1 MPa), respectively. The heat capacity and volume of Fluorinert, the heat capacity of 1-butanol, and the heat capacity and volume of the Neoflon were measured with the present apparatus. The heat capacity and volume of 3-methylpentane<sup>15</sup> and the volume of 1-butanol<sup>16</sup> were taken from the literature.

**D. Compressibility.** The sample volume was measured isothermally at several pressures in the range 0.1–10 MPa at several temperatures in the range 320–380 K for polystyrene and at 20–40 MPa and 235–260 K for OTP–OPP. The values of  $(\partial V/\partial P)_T$  were obtained as a function of pressure using the volume difference between each successive pressures. The values of  $(\partial V/\partial P)_T$  at 0.1 MPa (for polystyrene) and 28.8 MPa (for OTP–OPP) were determined by the extrapolation and interpolation of these data. The contribution from the pressure transmitting medium was subtracted by using the data measured

by this apparatus for Fluorinert and the literature data for 3-methylpentane.<sup>15</sup> The effects from the sample cup and the sealing device were neglected.

**E. Enthalpy and Volume Relaxation.** In the temperature-jump experiment, the sample was cooled rapidly at 20.8 MPa from 373 K ( $\sim T_g + 20$  K) down to 353 K ( $\sim T_g$ ) for polystyrene and at 28.8 MPa from 333 K ( $\sim T_{fus} + 20$  K) to 232 K ( $\sim T_g$ ) for OTP-OPP. The cooling rate was ca. 1.7 K min<sup>-1</sup> for the former and ca. 3 min<sup>-1</sup> for the latter. In the pressure-jump experiment, the sample was pressurized at 353 K from 0.1 to 20.8 MPa for polystyrene and at 232 K from 0.1 to 28.8 MPa for OTP-OPP. The pressurizing rate was ca. 10 MPa min<sup>-1</sup> for both samples.

The enthalpy relaxation of the sample was measured as the exothermic spontaneous temperature drift of the cell caused by the enthalpy released from the sample. The departure from the equilibrium configurational enthalpy at time  $t$  was calculated by

$$\Delta H_c(t) = [C_{tot}\{T(t_f) - T(t)\} - (dT/dt)_{hl}(t_f - t)]/w \quad (1)$$

where  $C_{tot}$  represents the total heat capacity excluding the configurational part of the sample,  $T$  the observed temperature of the cell,  $t_f$  the final time of the observation at which the relaxation has completed to within the precision of the measurement,  $(dT/dt)_{hl}$  the temperature-drift rate due to the heat leakage arising from slight incompleteness of the adiabatic control, and  $w$  the amount of the sample.

The volume relaxation of the sample was measured in the high-precision mode of the volume measurement system. The departure from the equilibrium configurational volume at time  $t$  was calculated by

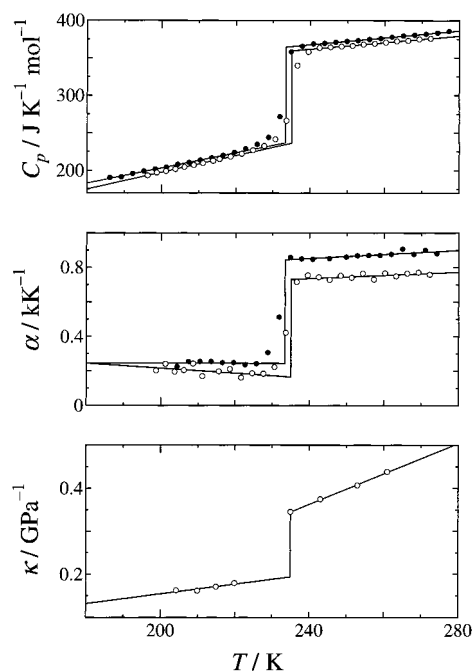
$$\Delta V_c(t) = \{V(t) - V(t_f)\}/w + \int_{t_f}^{t_f} [dV_{sr}^*/dT]\{dT(t)/dt\} dt/w \quad (2)$$

where  $V$  is the observed volume of the sample room and  $V_{sr}^*$  the volume of the sample room excluding the configurational part of the sample. The second term on the right-hand side of eq 2 corresponds to the correction for the thermal expansion caused by the temperature change due to the enthalpy relaxation. The magnitude of this term was ca. 10% of the first term.

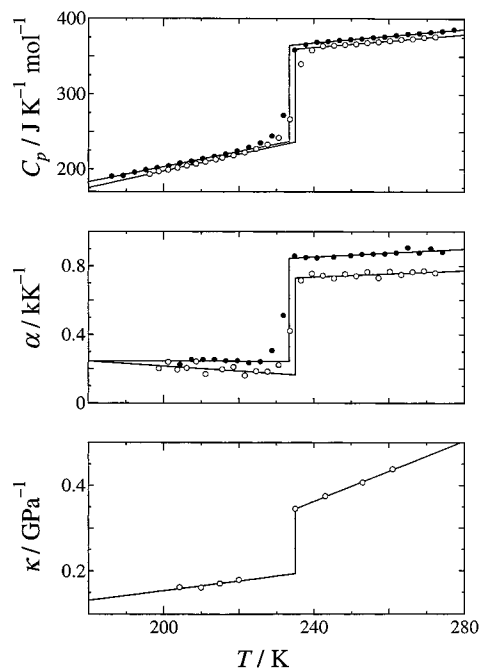
It took ca. 3 days to obtain constant temperature and volume drifts within the resolution of each measurement (temperature, 100  $\mu$ K; volume,  $2 \times 10^{-6}$  cm<sup>3</sup>) for both samples. As a reference experiment, the sample was rapidly cooled to the temperature where it was free from any relaxation processes (365 K for polystyrene and 250 K for OTP-OPP). It took ca. 30 min for polystyrene and 17 min for OTP-OPP to reach thermal equilibrium in the cell. In the measurement of the structural relaxation, therefore, the temperature and volume measurements were started at 30 min (for polystyrene) or 17 min (for OTP-OPP) after the rapid cooling.

### 3. Results and Discussion

**A. Heat Capacity, Thermal Expansivity, and Isothermal Compressibility.** Figures 3 and 4 show the plots of the heat capacities  $C_p$ , thermal expansivities  $\alpha$ , and isothermal compressibilities  $\kappa$  of polystyrene and OTP-OPP, respectively. A clear jump due to the glass transition occurred in all the curves. The solid straight lines represent the extrapolations of the data, which were used for the estimation of  $\Delta C_p$ ,  $\Delta\alpha$ , and  $\Delta\kappa$  at  $T_g$ .  $\Delta C_p$ ,  $\Delta\alpha$ , and  $\Delta\kappa$  of polystyrene (at 0.1 MPa) and OTP-OPP (at 28.8 MPa) thus determined are tabulated in Table 1. The



**Figure 3.** Heat capacities  $C_p$ , thermal expansivities  $\alpha$ , and isothermal compressibilities  $\kappa$  of polystyrene. The  $C_p$  and  $\alpha$  were measured at 0.1 MPa (●) and 20.8 MPa (○), and  $\kappa$  was determined as the value at 0.1 MPa by the extrapolation from the pressure vs volume data in the range 0.1–10 MPa. The solid straight lines represent the extrapolations of the data, which were used for the estimation of  $\Delta C_p$ ,  $\Delta\alpha$ , and  $\Delta\kappa$  at  $T_g$ .



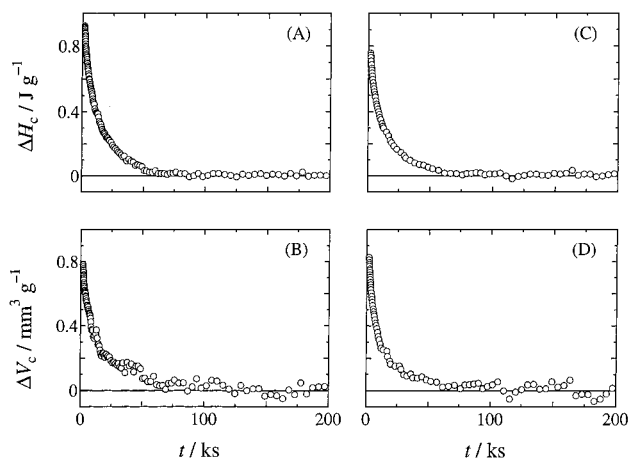
**Figure 4.** Heat capacities  $C_p$ , thermal expansivities  $\alpha$ , and isothermal compressibilities  $\kappa$  of OTP-OPP. The  $C_p$  and  $\alpha$  were measured at 0.1 MPa (●) and 28.8 MPa (○), and  $\kappa$  was determined as the value at 28.8 MPa by the interpolation from the pressure vs volume data in the range 20–40 MPa. The solid straight lines represent the extrapolations of the data, which were used for the estimation of  $\Delta C_p$ ,  $\Delta\alpha$ , and  $\Delta\kappa$  at  $T_g$ .

values for polystyrene agreed satisfactorily with the most reliable literature values<sup>17</sup> shown in parentheses in Table 1. The Prigogine-Defay ratios  $\Pi$  of polystyrene and OTP-OPP are also tabulated in Table 1. They are significantly larger than unity, indicating that more than one internal parameter is required to

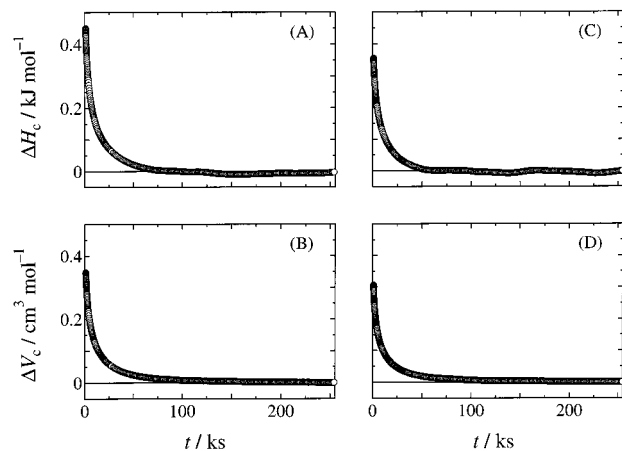
**TABLE 1: Thermodynamic Quantities Associated with the Glass Transition and the Prigogine–Defay Ratio**

	$T_g$ K	$\Delta C_p$ $J K^{-1} mol^{-1}$	$\Delta\alpha$ $kK^{-1}$	$\Delta\kappa$ $GPa^{-1}$	$V$ $cm^3 mol^{-1}$	$\Pi$
PS <sup>a</sup>	$353 \pm 0.3$	$34 \pm 2$ (30) <sup>b</sup>	$0.32 \pm 0.01$ (0.36) <sup>b</sup>	$0.16 \pm 0.01$ (0.19) <sup>c</sup>	$100.8 \pm 0.3$	$1.3 \pm 0.1$
OTP–OPP	$233.7 \pm 0.2$	$123 \pm 2$	$0.56 \pm 0.01$	$0.150 \pm 0.006$	$203.9 \pm 0.6$	$1.20 \pm 0.05$

<sup>a</sup> Quantities per monomer unit. <sup>b</sup> The most reliable literature value (ref 17). <sup>c</sup> The most reliable literature value (ref 8).



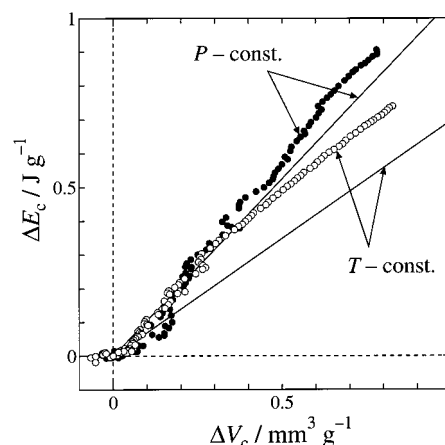
**Figure 5.** Relaxation of the enthalpy (upper graphs A and C) and volume (lower graphs B and D) of polystyrene, respectively. The data on the left-hand side, graphs A and B, were collected after the temperature jump and those in the right-hand side, graphs C and D, after the pressure jump. All the data were measured at 20.8 MPa and 353 K. The abscissa of the graph is the time  $t$ , and its origin is the time at which the jump process was finished.



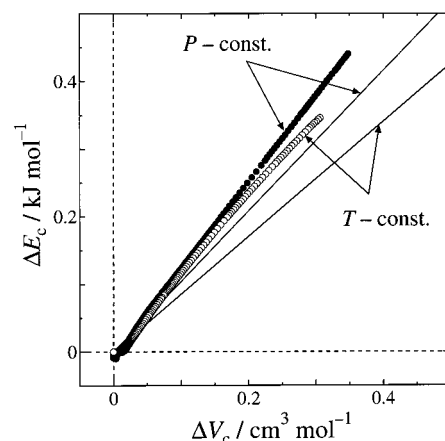
**Figure 6.** Relaxation processes of the enthalpy (upper graphs A and C) and volume (lower graphs B and D) of OTP–OPP, respectively. The data on the left-hand side, graphs A and B, were collected after the temperature jump and those on the right-hand side, graphs C and D, after the pressure jump. All the data were measured at 28.8 MPa and 232 K. The abscissa of the graph is the time  $t$ , and its origin is the time at which the jump process was finished.

describe the glassy state thermodynamically. This is consistent with the previous reports.<sup>12,18</sup>

**B. Enthalpy and Volume Relaxation.** Figures 5 and 6 show the relaxation processes of the enthalpy (upper graphs A and C) and volume (lower graphs B and D) of the polystyrene and OTP–OPP, respectively. The data on the left-hand side, graphs A and B, were collected after the temperature jump and those on the right-hand side, graphs C and D, after the pressure jump. The abscissa of the graph is the time  $t$ , and its origin is the time at which the jump process was finished. The present data are the first successful data of the simultaneous measurement of the enthalpy and volume relaxation near  $T_g$ . The points for



**Figure 7.** Relaxation paths in the configurational internal energy ( $\Delta E_c$ ) vs configurational volume ( $\Delta V_c$ ) planes of polystyrene observed at 20.8 MPa and 353 K. The closed and open circles denote the data after the temperature and pressure jumps, respectively. The relaxation proceeds from the upper right to the lower left in the graph and terminates at the origin corresponding to the equilibrium state. The solid lines represent the  $\Delta E_c$ – $\Delta V_c$  relation in the equilibrium states. These lines were calculated from the experimental data as described in the text.



**Figure 8.** Relaxation paths in the configurational internal energy ( $\Delta E_c$ ) vs configurational volume ( $\Delta V_c$ ) planes of OTP–OPP observed at 28.8 MPa and 232 K. The closed and open circles denote the data after the temperature and pressure jumps, respectively. The relaxation proceeds from the upper right to the lower left in the graph and terminates at the origin corresponding to the equilibrium state. The solid lines represent the  $\Delta E_c$ – $\Delta V_c$  relation in the equilibrium states. These lines were calculated from the experimental data as described in the text.

OTP–OPP (Figure 6) are less scattered than those for polystyrene (Figure 5). This is due to an improvement of the temperature control of the thermostat housing the manostat system, effected between the experiments on the two samples.

Figures 7 and 8 give the relaxation paths in the  $\Delta E_c$ – $\Delta V_c$  planes of polystyrene and OTP–OPP, respectively.  $\Delta E_c$  is configurational internal energy that can be related to  $\Delta H_c$  by the equation

$$\Delta H_c = \Delta E_c + P_0 \Delta V_c \quad (3)$$

where  $P_0$  is the pressure at which the relaxation is observed.



The discussion in the  $\Delta E_c - \Delta V_c$  plane is more illuminating than that in the  $\Delta H_c - \Delta V_c$  plane, since the equilibrium lines, i.e., the  $\Delta E_c - \Delta V_c$  relation in the equilibrium states, can be drawn easily by the equations

$$(\partial E_c / \partial V_c)_P = (\Delta C_p / (V \Delta \alpha)) - P \quad (4)$$

$$(\partial E_c / \partial V_c)_T = (T \Delta \alpha / \kappa) - P \quad (5)$$

for both the temperature jump at a constant pressure (eq 4) and the pressure jump at a constant temperature (eq 5). The curves calculated by using the experimental data of  $\Delta C_p$ ,  $\Delta \alpha$ , and  $\Delta \kappa$  at  $T_g$  are drawn in Figures 7 and 8. The relaxation proceeds from the upper right to the lower left in the graph and terminates at the origin corresponding to the equilibrium state.

The most interesting result of the present experiment is that the observed relaxation paths did not coincide with the equilibrium line for both polystyrene (a typical polymer glass) and OTP-OPP (a typical molecular glass) and for both temperature- and pressure-jump processes. This indicates that the fictive temperature concept does not apply satisfactorily to the structural relaxation even in the vicinity of equilibrium state. Since the sample was in an equilibrium state before the rapid cooling, the initial point of the relaxation path should lie on the equilibrium line. This means that the whole relaxation path in the  $\Delta E_c - \Delta V_c$  plane is not straight but convex, and initially, the volume relaxes faster than the enthalpy. Even though the present result has definitely shown that the relaxation path is not a string of equilibrium states, it is very important to determine the whole relaxation path in the  $\Delta E_c - \Delta V_c$  plane experimentally. For this purpose, the improvement of the apparatus and more advanced data analysis (e.g., deconvolution of the structural relaxation and thermal equilibration allowing for temperature distribution in the cell) are necessary to obtain the relaxation data within 15 min of the rapid cooling.

For further discussion of the relaxation path, a number of different relaxation paths should be determined experimentally. The relaxation measurements after much more rapid cooling are desirable for the determination of the paths that are much

different from the present one. It is also important to examine other glass-forming systems. By collection of data for different relaxation paths, it will be possible to identify the internal thermodynamic parameters that govern the progress of the structural relaxation in the glassy states. Gupta's multiparameter theory,<sup>19</sup> in which the fictive temperature and the fictive pressure are taken as the internal parameters, is the first one to be tested.

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## References and Notes

- (1) Recent reviews are as follows. Ediger, M. D.; Angell, C. A.; Nagel, S. R. *J. Phys. Chem.* **1996**, *100*, 13200. Angell, C. A. *Science* **1995**, *267*, 1924. Stillinger, F. H. *Science* **1995**, *267*, 1935. Frick, B.; Richter, D. *Science* **1995**, *267*, 1939. Hodge, I. M. *Science* **1995**, *267*, 1945. Greer, A. L. *Science* **1995**, *267*, 1947. Hunt, A. *J. Non-Cryst. Solids* **1993**, *160*, 183.
- (2) Takeda, K.; Yamamuro, O.; Suga, H. *J. Phys. Chem. Solids* **1991**, *52*, 607.
- (3) Fujimori, H.; Adachi, Y.; Oguni, M. *Phys. Rev. B* **1992**, *46*, 14501.
- (4) Randell, R. W.; Ngai, K. L.; Fong, G. R.; Aklonis, J. J. *Macromolecules* **1987**, *20*, 1070.
- (5) Kovacs, A. J. *Fortschr. Hochpolym.-Forsch.* **1963**, *3*, 394.
- (6) Scherer, G. W. *J. Am. Ceram. Soc.* **1984**, *67*, 504.
- (7) Adachi, K.; Kotaka, T. *Polym. J.* **1982**, *14*, 959.
- (8) Tribone, J. J.; O'Reilly, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 837.
- (9) Yamamuro, O.; Takahara, S.; Suga, H. *J. Non-Cryst. Solids* **1995**, *183*, 144.
- (10) Tool, A. Q.; Eichlin, C. G. *J. Am. Chem. Soc.* **1931**, *54*, 491.
- (11) Prigogine, I.; Defay, R. *Chemical Thermodynamics*; Longmans Green: New York, 1954.
- (12) Gupta, P. K.; Moynihan, C. T. *J. Chem. Phys.* **1976**, *65*, 4136.
- (13) Dixon, P. K.; Nagel, S. R. *Phys. Rev. Lett.* **1988**, *61*, 341.
- (14) Takahara, S.; Yamamuro, O.; Ishikawa, M.; Matsuo, T.; Suga, H. *Rev. Sci. Instrum.* **1998**, *69*, 185.
- (15) Oguni, M.; Watanabe, K.; Matsuo, T.; Suga, H.; Seki, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 77.
- (16) Zander, A. *Liebigs Ann. Chem.* **1882**, *214*, 138.
- (17) Oels, H. J.; Rehage, G. *Macromolecules* **1977**, *10*, 1036.
- (18) Moynihan, C. T.; Lesikar, A. V. *Ann. N.Y. Acad. Sci.* **1981**, *371*, 151.
- (19) Gupta, P. K. *J. Non-Cryst. Solids* **1988**, *102*, 231.