

Vibrational and configurational specific heats during isothermal structural relaxation of a glass to equilibrium liquid

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To determine the effect of isothermal structural change on the configurational and vibrational parts, the real component of the complex specific heat C'_p of poly(styrene) at 3.33 mHz frequency was measured in its vitrification range during very slow cooling, heating, and during the isothermal annealing of its glassy state formed by rapid cooling. As the structure relaxes during annealing, C'_p decreases asymptotically with time by at least 1%. This is attributed to mostly a decrease in the configurational contribution to C'_p as the relaxation time of the α process increases and contributions from the Johari-Goldstein relaxation decrease. C'_p of the structurally equilibrated state is closer to the vibrational C_p than the C'_p for 3.33 mHz frequency measured for the slowest cooling at 1 K/h. The apparent specific heat $C_{p,app}$ was also measured during cooling and heating of the annealed and the unannealed samples, and the data were analyzed in terms of the enthalpy loss and recovery with the spontaneously changing fictive temperature. A procedure is described for determining when the equilibrated state has been reached. The vibrational C_p is not greatly affected by the structural change toward equilibrium. Thus the configurational C_p is equal to the difference between the equilibrium liquid's and the nonequilibrium glass C_p . Consequences of thermoviscoelastic effects on the specific-heat spectroscopy have been discussed.

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I. INTRODUCTION

The structure of a liquid varies with the temperature T . The consequent variation in its energy, entropy, and volume causes its configurational and vibrational parts of the specific heat $C_{p,conf}$ and $C_{p,vib}$ to vary with T . In the glassy state, the structure becomes fixed and the configurational part ceases to change with T , but the vibrational part continues to change due to change in the phonon frequency as for a crystal. These effects have been discussed and computer simulated using the concepts of the potential-energy landscape,¹⁻⁴ but it had been difficult to determine the configurational and vibrational parts by an experiment. Recently,⁵⁻⁷ $C_{p,vib}$ and $C_{p,conf}$ of an equilibrium melt were determined by measuring C'_p , the real component of the complex specific heat at a fixed frequency in the linear-response regime of the temperature modulation. In those experiments, the liquid was cooled and heated at a rate slow enough that the measurement temperature T was the same as the fictive temperature T_f , i.e., the state remained in an internal equilibrium. In this case, C'_p is equal to the *unrelaxed* or $C_{p,vib}$ in the absence of high-frequency relaxation of the equilibrium melt provided that $(\omega\tau_{cal})^2 \gg 1$, ω being the temperature-modulation frequency and τ_{cal} the calorimetric relaxation time. The time-dependent specific heat $C_{p,app}$ of the nonequilibrium state was also measured in order to estimate the onset temperatures of structural freezing on cooling and structure unfreezing on heating and to determine $C_{p,app}$ of the nonequilibrium glassy state at $T < T_f$. The findings contradicted an argument-based conclusion that vibrational C_p increases in a sigmoid-shape manner when a glass is heated through its softening range to an ultraviscous liquid and that the configurational C_p is much less than the difference, ΔC_p , between the equilibrium melt and the extrapolated glassy state C_p .

The structure of a glass also spontaneously relaxes with time isothermally to the structure of an equilibrium liquid of lower volume, energy, and entropy. During this occurrence, both $C_{p,conf}$ and $C_{p,vib}$ decrease. Thus an equilibrium state characterized by $T_f = T$ can be reached also by isothermally annealing a glass at a temperature T . During this process, its structure spontaneously relaxes, and its T_f decreases to T asymptotically with time.⁸ In this experiment, a high- T_f glass may be made by relatively rapid cooling of a melt and its C'_p measured in the linear-response range during isothermal annealing. Moreover, if cooling is done at slow enough rate that the structure does not kinetically freeze, C'_p measured in the linear-response range of temperature modulation would decrease until the equilibrium melt's unrelaxed C'_p or $C_{p,vib}$ value is reached provided that $(\omega\tau_{cal})^2 \gg 1$. But if cooling is not slow enough and the structure becomes kinetically frozen, C'_p would be measured for the nonequilibrium (glassy) state. The nonequilibrium state would structurally relax on isothermal annealing until T_f is equal to T , and the magnitude of the decrease in C'_p would correspond only to the effect of the structural change. Also C'_p of the internally equilibrated state for $(\omega\tau_{cal})^2 \gg 1$ condition may be compared against the C'_p and $C_{p,app}$ of the glassy state to determine whether the internal equilibrium achieved by heating a glass to its melt state makes a considerable difference in the vibrational and configurational parts ($C_{p,vib}$ and $C_{p,conf}$) as done earlier.⁵⁻⁷ Here, we use these approaches to investigate the changes in $C_{p,vib}$ and $C_{p,conf}$ with the structural change.

We had studied the decrease in C'_p during the annealing of the glassy state of triphenylolmethane triglycidyl ether (TPTGE) (Ref. 9) and attributed the effect to several time- and temperature-dependent irreversible processes. The effect observed was complicated because intermolecular hydrogen bonds and ion pairs form (exothermally) in TPTGE and their

equilibrium constant and population varies with T . Thus there was an additional contribution to the temperature-dependent enthalpy of its glassy state and hence to C_p , which adds to the complexity of the potential-energy landscape description.^{1–4} Here we chose to study poly(styrene) as an example of a glass in which hydrogen bonds and ions are absent. Schick and co-workers¹⁰ studied the glass-liquid dynamics of poly(styrene) by using normalized C'_p and $C_{p,app}$ with a focus on the quantitative relation between the endotherm in the $C_{p,app}-T$ plot and the relaxing feature of the C'_p-T plot. Here, we also discuss the differences between $C_{p,app}$ and C'_p and show that the unrelaxed C'_p of the equilibrium melt is significantly less than $C_{p,app}$ of its glassy state. Finally we discuss how the consequences of the decrease in C'_p on conversion of a glass on isothermal annealing to the equilibrium state bear upon our understanding of the vibrational and configurational parts of C_p . A discussion of the configurational and vibrational specific heats in a historical context is given in Refs. 5–7.

II. EXPERIMENTAL METHODS

Poly(styrene) of $M_w=212.4 \times 10^3$ and $M_n=200.6 \times 10^3$ Daltons was purchased in granulated powder form from Sigma-Aldrich Chemicals and was stored in dry atmosphere. The technique of temperature-modulated scanning calorimetry (TMSC) for dynamic C_p measurements has been well established.^{10–17} Briefly, the sample holder is kept inside the calorimetric cell,¹⁸ which is surrounded by a thermal shield that ensures a uniform spatial distribution of the temperature along the 90 mm length of the sample holder within ± 0.05 K of the average temperature, which in turn is measured by the thermal sensors distributed along the entire surface of the cell. The instrument was calibrated by using dodecane as a standard liquid and absolute value of C_p was thus determined. Measurements made with different samples showed a reproducibility of better than 0.5%. The reproducibility of C'_p was better than 0.1% for the repeat measurements when the sample remained in the calorimeter. The instrument has been used in different type of studies earlier.^{19–23} We used it in the temperature-modulation mode to determine the complex specific heat $C_p^*(=C'_p+iC''_p)$ and in the usual scanning mode to determine $C_{p,app}$ only.

Poly(styrene) powder was placed inside a 2.2 mm internal diameter, 90-mm-long, and 0.3-mm-thick-wall glass capillary closed at one end and its mass (~ 100 mg) was accurately determined. It was hermetically sealed by fusing its open end by using a directed thin flame. The sample holder was then inserted into the calorimeter cell and allowed to come to a constant temperature of 393 K. A sinusoidal temperature modulation of 1 K peak-to-peak amplitude and 3.33 mHz frequency ($\omega=20.9$ mrad/s or oscillation period of 300 s) was superposed on the cooling and heating ramps. The sample was cooled at 1, 12, and 60 K/h rates in different experiments and heated at the same rates. These are 1/10 to 1/600 of the 10 K/min (600 K/h) rate and even less for the 20 K/min (1200 K/h) rate normally used in differential scanning calorimetry (DSC) studies. The time duration of each experiment was about 3 h to several days. (In contrast, a usual DSC

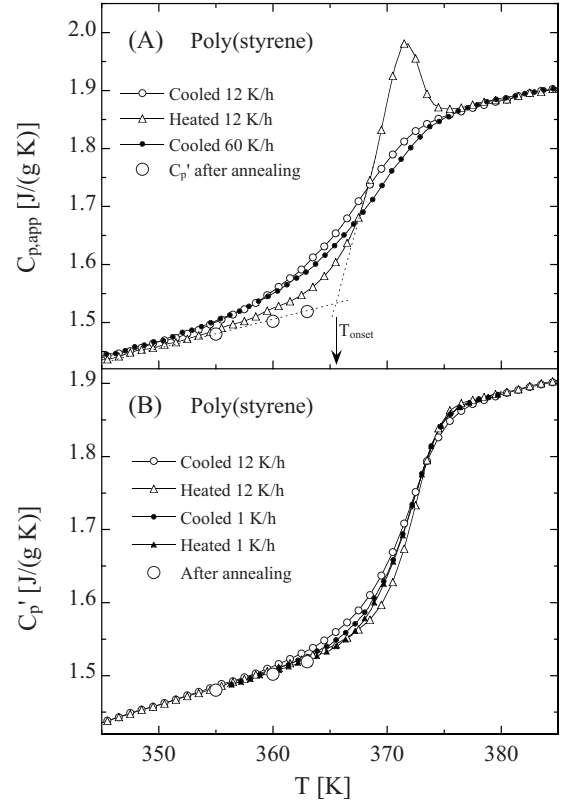


FIG. 1. (A) The plots of $C_{p,app}$ against T measured during cooling from 393 to 333 K and thereafter heating of poly(styrene) to 393 K at 12 K/h rate. Also shown is the plot of $C_{p,app}$ for the sample cooled at 60 K/h rate from 393 to 345 K. (B) The corresponding plots of C'_p measured at 3.33 mHz during cooling and thereafter heating at 12 K/h. The temperature range 345–385 K is sufficient to show the features of the structural relaxation. The large circles in both panels denote the C'_p value reached after annealing at fixed temperatures of 355, 360, and 363 K.

takes 8–10 min for 10 K/min rate scan and 4–5 min for the 20 K/min rate. The long duration experiments performed here also required greater sensitivity and stability, which was a special feature of this calorimeter.) Formalism for analyzing the C'_p and C''_p data has been provided earlier.²¹

III. RESULTS

Figure 1(A) shows the plots of $C_{p,app}$ against T measured during cooling from 393 to 333 K and thereafter heating to 393 K at 12 K/h. The two plots do not coincide because of the time-dependent nature of kinetic freezing and unfreezing of the structure as is well known for structural freezing and unfreezing.^{8,10,16,17} The onset temperature, T_{onset} , of the sigmoidal-shape $C_{p,app}$ -rise for 12 K/h heating is 365.7 K. This is *not* the usual T_g that is defined as the endotherm's T_{onset} for the heating rate of 600 K/h (10 K/min) or 1200 K/h (20 K/min). Also shown in Fig. 1(A) is $C_{p,app}$ measured during the cooling from 393 to 345 K at 60 K/h.

Although both C'_p and C''_p were measured, only the plots of C'_p measured simultaneously with $C_{p,app}$ [Fig. 1(A)] at 12 K/h rate are shown in Fig. 1(B). (As expected, the corre-

sponding C_p'' plots showed a peak at T near the point of inflexion in the C_p' plot. An analysis of the C_p'' data will be discussed in connection with the calorimetric relaxation of the rubber state of polystyrene in a different context.) The cooling and heating plots of C_p' also do not coincide in the temperature range of their sigmoid shape. This indicates that the 12 K/h rate is not low enough to maintain the sample in an internal equilibrium below a certain T , and a lower rate is needed to maintain it in an equilibrium. ^{5,7,10,16} The resulting difference between the two C_p' has been found to decrease as the cooling and heating rates are decreased and the feature itself gradually vanishes. ^{5,7,10,16} For the limiting low cooling and heating rates, the two C_p' plots would coincide throughout the measurement range. To investigate the extent to which that occurs and to determine the magnitude of the C_p' change at low temperatures, a further experiment was performed in which C_p' was measured during the cooling and heating at 1 K/h rate. These plots are included in Fig. 1(B). It is evident that the difference between the two C_p' values at the same T is greatly reduced. It is also notable that C_p' decreases apparently linearly with decreasing T in the 345–360 K range. This is an artifact of the manner of plotting and of the fact that the cooling rate determines the slope at these temperatures. Annealing is expected to decrease C_p' in this range more at higher than at lower T , which would make the plot nonlinear. But the annealing period needed to observe this by reaching an equilibrium state would be longer than 12 h at 363 K.

Five experiments were performed in which the sample was cooled from 393 K to the annealing temperature T_{ann} at 60 K/h rate and kept at T_{ann} for a period t_{ann} during which its C_p' was measured at regular intervals. The conditions were: (i) T_{ann} of 355 K and t_{ann} up to 83 ks (23 h); (ii) T_{ann} of 360 K and t_{ann} up to 120 ks (33 h); (iii) T_{ann} of 360 K and t_{ann} up to 446 ks (124 h); (iv) T_{ann} of 363 K and t_{ann} of up to 120 ks (33 h); and (v) T_{ann} of 363 K and t_{ann} of up to 240 ks (67 h). In all cases the $C_{p,\text{app}}$ measured during the cooling at 60 K/h to the T_{ann} coincided with the data in Fig. 1(A). The C_p' reached after the annealing is denoted by large circles in Fig. 1(B), and the C_p' measured during the annealing period is plotted against $\log_{10}(t_{\text{ann}})$ in Fig. 2.

After these measurements, the annealed sample from each experiment (i), (iii), and (v) was heated at 12 K/h rate from its respective T_{ann} of 355, 360, and 363 to 393 K and its $C_{p,\text{app}}$ and C_p' were measured. The $C_{p,\text{app}}-T$ plots are shown in Fig. 3(A). The corresponding plots of C_p' are shown in Fig. 3(B).

Before the discussion, it may help to note some general features of glass formation and the dynamic specific heat: (i) The complex C_p measurement requires the amplitudes of modulated heat flow and temperature and the phase difference between them in a linear-response approximation, and not the heat input and the net temperature change as for measuring C_p . (ii) Structural freezing temperature is determined by the cooling rate and not by the probe frequency. Increase in the probe frequency for a fixed cooling rate does not upshift this temperature: only increasing the cooling rate does so. (iii) The structure may kinetically freeze below the temperature at which τ_{cal} exceeds $1/\omega$ for a low cooling rate. This allows us to find a cooling/heating rate and a tempera-

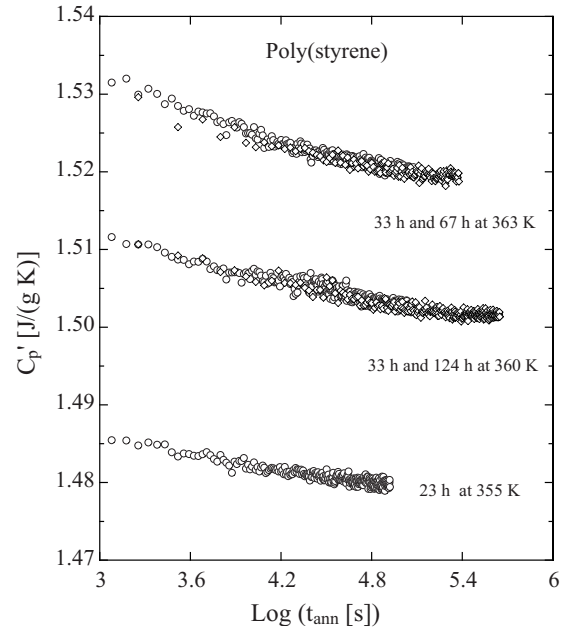


FIG. 2. The plots of C_p' against the annealing time measured when poly(styrene) was kept at 355, 360, and 363 K in five separate experiments. For each experiment, the sample was cooled from its equilibrium state at 393 K at 60 K/h to T_{ann} . The C_p' reached after the annealing in these experiments is shown by large circles in Fig. 1(B).

ture range in which an equilibrium liquid's unrelaxed C_p' can be measured for a given ω . (iv) Increasing ω bodily shifts the sigmoid region of the C_p' plot to a higher T range at which τ_{cal} is less, but the structural freezing temperature does not change. (v) The $C_p'-T$ plots measured during the heating and the cooling coincide as long as $T=T_f$. But as the structure begins to kinetically freeze or T_f to deviate from T , the plots separate. (vi) When the cooling and heating rates are decreased, the temperature interval and the extent of the separation between the plots gradually decrease and vanish from the measurement range. For the limiting low cooling and heating rates, the two C_p' plots coincide throughout the measurement range. (vii) For lower heating rates, the T_f and C_p' of the glass are lower because decrease in T_f increases τ_{cal} . (viii) Since T_g is defined for heating rates of 10 to 20 K/min (600 to 1200 K/h), our $C_{p,\text{app}}$ measurements do not yield *that* T_g or *that* glass structure. Instead, they yield a structural freezing (unfreezing) temperature, which is lower than that T_g . (ix) One measures $C_{p,0}$, the zero frequency or relaxed value of C_p for the condition $(\omega t)^2 \ll 1$, and the unrelaxed C_p or $C_{p,\text{vib}}$ when $(\omega t)^2 \gg 1$. For $\omega\tau$ values between these two extremes, there is a phase lag between the structural enthalpy response and the temperature modulation. This is analogous to dielectric relaxation in which the sample is electrically polarized to determine the polarization itself and there is a frequency-dependent phase lag in the response. Thus one measures C_p' and C_p'' of an equilibrium state even when the long τ_{cal} prohibits measurements of $C_{p,0}$ or the full relaxation spectra, and instrument limitations for ω allow only experiments for only the high-frequency side of the spectrum. (x) As for the volume and enthalpy, C_p' and C_p'' of a nonequilib-

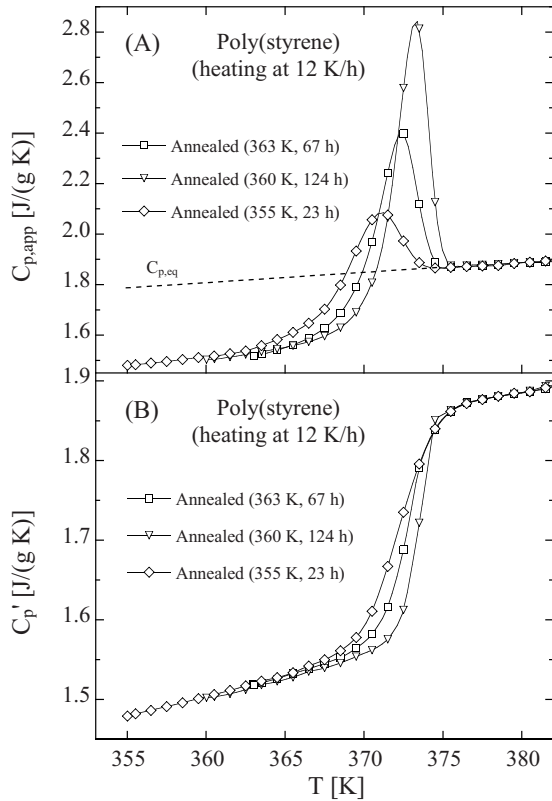


FIG. 3. (A) The plot of $C_{p,app}$ against T measured during the heating of poly(styrene) at 12 K/h after annealing for 23 h at 355 K, 124 h at 360 K, and 67 h at 363 K. The dashed line is for the extrapolated $C_{p,0}$, which is the relaxed C_p . (B) The corresponding plots of C_p' against T .

rium state change on annealing as the structure changes until an internal equilibrium state is reached and $T_f = T$. (xi) For the same cooling/heating rates, T_{onset} of the $C_{p,app}$ endotherm is far below the onset temperature of the C_p' sigmoid-shape plot.

In addition, we point out that there is an occasional misconception in the study of supercooled liquids, namely, that a liquid at a given temperature is seen as a glass at a measurement frequency such that $(\omega t)^2 \gg 1$. This is *not* the case: A liquid only behaves like a rigid glass in as much as its properties at high ω are similar to the properties of its glass. For example, velocity of propagation of ultrasonic or hypersonic waves in an ultraviscous liquid is *not* the velocity of propagation in its rigid (nonequilibrium) glass, even when the imaginary component of the shear modulus at these frequencies approaches zero. It should also be stressed that there is no single or unique glassy state. Different rates of cooling a liquid produce different glassy states each with its own properties. Also, structural relaxation produces different glassy states, which are described in terms of glasses of different fictive temperatures. Moreover, calorimetric relaxation studies of thermal cycling of the rigid glassy state have shown that each mode of molecular or atomic motion in the distribution of relaxation times kinetically freezes at a temperature that is determined by its own time scale, thereby indicating a miniglass transition for each such mode.^{24,25} Therefore, some of the faster modes of motion remain unfrozen even in the

glassy state. Also, glasses made by cooling under a high pressure and then released to 1 bar pressure differ from those produced by cooling at 1 bar pressure.

During annealing of a glass, (i) the average relaxation time increases, which bodily shifts the C_p' spectra to lower frequencies, and (ii) faster modes in the relaxation-time distribution kinetically freeze. These two effects may be distinguished by measuring the enthalpy recovery on thermal cycling of an annealed and unannealed sample in a temperature range in which it remains in the rigid glassy state. Such measurements^{24,25} have shown that when the enthalpy difference of the annealed and unannealed sample is plotted against T , a monotonic increase with T appears when occurrence (i) dominates, and a peak appears when occurrence (ii) dominates.

IV. DISCUSSION

A. Apparent and equilibrium specific heat

Increase in $C_{p,app}$ of poly(styrene) during heating has been studied several times by using the bulk samples,^{10,26} nanometer size layers^{27,28} and nanometer thick films by ultrafast calorimetry.²⁹ The difference between these and our studies is that (i) $C_{p,app}$ has been measured during both the cooling and the heating, and (ii) cooling rates are 100 to 1000 times slower than in the usual DSC measurement, which allowed us to measure the relaxation spectra at low temperatures where the distribution of relaxation times is broad. Temperature dependence of its dynamic C_p has also been studied and compared against its $C_{p,app}$ features for obtaining the best fit of the structural relaxation models.¹⁰

In Fig. 1(A), the $C_{p,app} - T$ plots show the well-known effects of spontaneous relaxation that causes $C_{p,app}$ to become time dependent, broadens the sigmoid-shape region during the cooling, causes the cross over of the plots, and produces an “overshoot” on heating.^{8,10,30,31} The last one appears as an increase in $C_{p,app}$ above the $C_{p,0}$ to a peak value at 372 K and then a decrease to $C_{p,0}$. To describe these effects, we recall that $C_{p,app}$ is the sum of $C_{p,vib}$ and the configurational part $C_{p,conf}$. As a liquid’s structure varies with T , its $C_{p,0}$ varies mainly because both $C_{p,conf}$ and $C_{p,vib}$ vary with the structure. In addition, $C_{p,vib}$ varies with T because the phonon frequency varies when different vibrational energy levels are occupied with changing T within the unchanging distribution of the available characteristic frequencies determined by the structure. $C_{p,conf}$ and $C_{p,vib}$ decrease together on cooling until the liquid vitrifies. Both are time dependent in the sigmoid-shape region of the $C_{p,app}$ plots.

In general, $C_{p,app}$ of the glassy state decreases on cooling because of (i) the decreasing contributions from the faster modes in the distribution of the (calorimetric) α -relaxation process,³² (ii) the decreasing strength of the localized or Johari-Goldstein (JG) relaxation,^{33–36} (iii) the increasing phonon frequency, and (iv) the decreasing vibrational amplitude and hence the anharmonic effects.³⁶ Among these (i) seems to dominate at T immediately below the usual T_g .^{24,25} Thus the generally positive value of $(dC_{p,app}/dT)$ decreases rapidly on cooling immediately from this T_g and slowly at lower T . For a given material, $(dC_{p,app}/dT)$ would be higher

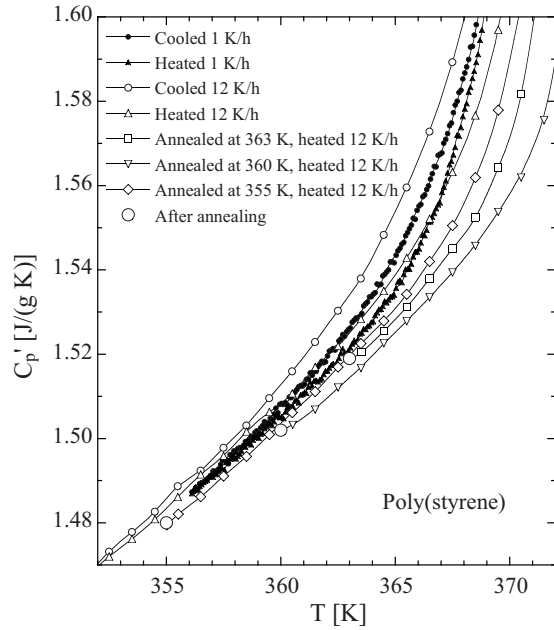


FIG. 4. The plot of C_p' against T measured for heating and cooling poly(styrene) at 1 K/h and 12 K/h rates shown at an enlarged scale. Also shown are the corresponding plots for heating of the three annealed samples at 12 K/h.

when a glass is made by rapid cooling and lower when it is made by slow cooling. Among different materials, $(dC_{p,\text{glass}}/dT)$ would be higher if the distribution of relaxation times is broader.

We now consider the $C_p'-T$ plots in Fig. 1(B). At T above the sigmoid-shape range, $\omega\tau_{\text{cal}} \ll 1$. Therefore, here C_p' is equal to $C_{p,0}$, the zero frequency or relaxed C_p . Poly(styrene) is a P-type melt, i.e., its $(dC_{p,0}/dT)$ is positive; i.e., the sum of its $C_{p,\text{conf}}$ and $C_{p,\text{vib}}$ increases with T . As mentioned earlier here, when the cooling and heating rates are slow enough to maintain internal equilibrium, C_p' measured during cooling is the same as that measured during the heating. But when the rates are not slow enough, the values differ and the $C_p'-T$ curve crosses in the sigmoid-shape range as in Fig. 1(B). This is prominently seen for 12 K/h rate but it occurs also for the 1 K/h rate. Therefore, the melt's structure in our study kinetically froze even for 1 K/h rate, and the conditions for determining the *unrelaxed* C_p' of the *equilibrium* state was not achieved. To investigate it in detail, C_p' is plotted on an enlarged scale in Fig. 4, which shows that for 1 K/h rate the maximum difference between the cooling and heating curves is less than 0.6 % of the C_p' value. For $(\omega\tau_{\text{cal}})^2 \gg 1$, therefore, the *unrelaxed* C_p' of the equilibrium melt becomes as expected less than the measured C_p' of the kinetically frozen state. Ultimately, in the glassy state at $T < 360$ K, C_p' for 1 K/h rate is only 0.2% less than the C_p' measured for 12 K/h rate. If faster modes of a distribution of relaxation times or the JG relaxation were to contribute to C_p' , its apparently unrelaxed value would be slightly higher than $C_{p,\text{vib}}$ of the equilibrium melt, i.e., the distribution of relaxation times and the JG relaxation tend to compromise accurate determination of $C_{p,\text{vib}}$. Nevertheless, the difference between the two values is no more than 1%. We maintain this uncertainty in further discussion.

The calorimetric relaxation of poly(styrene) has a distribution of relaxation times and there is also a relatively small JG relaxation. Since contributions from both decrease on annealing, the equilibrium state's C_p' is accurately determined only after the sample has relaxed isothermally to maximize their decrease.

B. Decrease in the specific heat on annealing

In Fig. 2, C_p' decreases asymptotically with t_{ann} during isothermal annealing in a manner characteristic of a stretched exponential decay. Since annealing decreases T_f toward T , the shape of the plot is qualitatively similar to the shape of the T_f against $\log(t_{\text{ann}})$ plot. The decrease in C_p' has been attributed to the loss of both the vibrational and configurational contributions and in that sense it corresponds to a decrease in the enthalpy and entropy of a glass and hence to a decrease in the residual entropy. As mentioned here earlier, the overall decrease in C_p' is due to decrease in four interdependent contributions,

$$C_p'(t_{\text{ann}}) = C_{p,\alpha}'(t_{\text{ann}}) + C_{p,\text{JG}}(t_{\text{ann}}) + C_{p,\text{vib}}(t_{\text{ann}}) + C_{p,\text{anh}}(t_{\text{ann}}), \quad (1)$$

where $C_{p,\alpha}'$ contains all contributions from the α -relaxation process at the relevant frequency, $C_{p,\text{JG}}$ is the contribution from the JG relaxation, which at this T and ω makes the full contribution, $C_{p,\text{vib}}$ is the phonon contribution, and $C_{p,\text{anh}}$ is the contribution from anharmonic forces both being only structure dependent. As the density increases on structural relaxation, τ_{cal} increases, which shifts the C_p' spectra to lower frequencies, and thus its contribution to $C_{p,\alpha}'$ at 3.3 mHz frequency decreases, $C_{p,\text{JG}}$ decreases as the number in the group of atoms or molecules contributing to the JG relaxation decreases, $C_{p,\text{vib}}$ decreases as the phonon frequency increases, and $C_{p,\text{anh}}$ decreases. There is a competitive effect from the increase in the magnitude of the (calorimetric) α process on densification during annealing. But its effect on $C_{p,\alpha}'$ is much smaller than the effect of increase in τ_{cal} . Since structural relaxation on annealing reduces $C_{p,\alpha}'$ and $C_{p,\text{JG}}$, it brings the C_p' closer to the sum of $C_{p,\text{vib}}$ and $C_{p,\text{anh}}$.

To compare the effect of annealing on C_p' against the effect of cooling or heating to the same T , we show in Fig. 4 the enlarged scale plots in the low T range for C_p' measured during cooling and heating the sample at 1 and 12 K/h, the C_p' value that was reached after annealing isothermally at their respective T_{ann} , and the C_p' that was measured during the heating of the annealed samples at 12 K/h rate. It shows that isothermal annealing at 355, 360, and 363 K decreases C_p' to a value less than the C_p' measured for the 12 K/h heating and cooling rates and even to a value measured for 1 K/h rate. To understand it, we consider that τ_{cal} of the state attained after annealing is much longer than of the unannealed nonequilibrium state at the same T that is obtained by cooling or heating, and the increase in τ_{cal} decreases C_p' more than any other change on annealing.

We now consider whether or not the equilibrium state of poly(styrene) was reached in our annealing experiments. We recall that as a glass structurally relaxes during the course of heating, its T_f decreases in a time-dependent manner as T

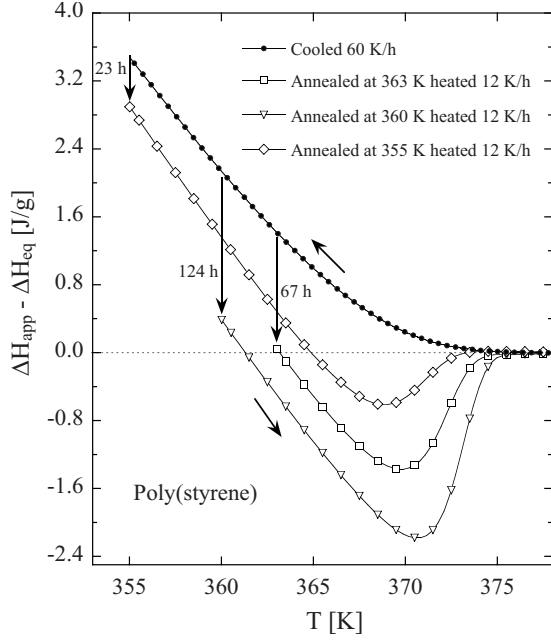


FIG. 5. The enthalpy change $[\Delta H_{\text{app}} - \Delta H_{\text{eq}}]$ calculated from the area of the $(C_{p,\text{app}} - C_{p,0})$ against T plots using the extrapolated $C_{p,0}$ shown in Fig. 3(A). The plots are for heating of the isothermally annealed poly(styrene) at 12 K/h rate. The plot for 60 K/h rate is only for cooling.

increases, and at a certain instant its T_f becomes equal to T . If heating is discontinued at that instant, the state remains at internal equilibrium and its $C_{p,0}$, if measured by a long-time experiment, would be higher than that of the glassy state. In contrast, if the heating is continued, the state point lies below the equilibrium line. On further heating it approaches the equilibrium line in a time and temperature-dependent manner from below, $C_{p,\text{app}}$ shows an overshoot, and the enthalpy and entropy of the equilibrium state are recovered. For comparison, in an isothermal annealing at a temperature T , structural relaxation decreases T_f ultimately to T and if the sample is heated thereafter, its state also approaches the equilibrium line from below, $C_{p,\text{app}}$ shows an overshoot, and the enthalpy and entropy are recovered. We use this as criteria for determining if the equilibrium state of $T_f = T$ has been reached on isothermal annealing, and for this purpose we determine the enthalpy change on heating after annealing from the difference between the areas of the $C_{p,\text{app}} - T$ plots shown in Fig. 3(A),

$$\Delta H_{\text{app}} - \Delta H_{\text{eq}} = \int_{398 \text{ K}}^T (C_{p,\text{app}} - C_{p,0}) dt, \quad (2)$$

where $C_{p,0}$ is the equilibrium state value obtained by linear extrapolation of the $C_{p,\text{app}}$ plot to T below 378 K as shown by the dashed lines in Fig. 3(A). For $T < T_f$, ΔH_{app} is higher than ΔH_{eq} , and the enthalpy change is positive. For $T > T_f$ the enthalpy change is negative, and for $T = T_f$ the enthalpy change is zero or $\Delta H_{\text{app}} = \Delta H_{\text{eq}}$. Only when T_f has reached T after isothermal annealing, heating of poly(styrene) would show a negative $\Delta H_{\text{app}} - \Delta H_{\text{eq}}$. Figure 5 shows the plots of the calculated $\Delta H_{\text{app}} - \Delta H_{\text{eq}}$ against T , where the data ob-

tained on cooling at 60 K/h are also given; the vertical arrows show the decrease in ΔH_{app} on annealing at T_{ann} of 355, 360, and 363 K for the periods indicated. The other three plots beginning at the respective T_{ann} are for heating the annealed sample at 12 K/h rate. It is evident that only for annealing at 363 K, T_f becomes equal to T and the state is in internal equilibrium. For the other two, $T_f > T$ and the state is not in internal equilibrium.

C. Vibrational and configurational specific heats

The unrelaxed C'_p of the equilibrium state for the condition $(\omega\tau_{\text{cal}})^2 \gg 1$, although indistinguishable from $C_{p,\text{vib}}$, is not formally equal to it because C'_p contains a small contribution from the first two terms on right-hand side of Eq. (1). The relaxed C'_p or $C_{p,0}$ of the melt for the condition $(\omega\tau_{\text{cal}})^2 \ll 1$ is equal to $C_{p,\text{vib}} + C_{p,\text{conf}}$ because now all the terms in Eq. (1) make full contribution to C_p . As the difference between $C_{p,0}$ and the unrelaxed C'_p of the equilibrium melt is equal to $C_{p,\text{conf}}$, measurements of C'_p alone seem sufficient for determining $C_{p,\text{conf}}$ provided that the sample's unrelaxed C'_p is measured in the equilibrium state.

We now compare at 363 K, $C_{p,\text{glass}}$ for the 12 K/h heating rate against C'_p reached after annealing in Fig. 1(A). The difference is positive and small and it has been attributed to a longer τ_{cal} of the state for which C'_p , which is equal to $C_{p,\text{vib}}$, is measured. Moreover, this C'_p is close to the extrapolated $C_{p,\text{glass}}$, and there is no step-like rise from $C_{p,\text{glass}}$ to $C_{p,\text{vib}}$ of the equilibrium liquid. Evidently, the vibrational contribution does not greatly increase when the glass structure kinetically unfreezes on heating and becomes an equilibrium melt. Therefore, we conclude that $C_{p,\text{conf}}$ is equal to ΔC_p within the measurement errors.

One purpose of this study was to use a procedure for determining the difference between $C_{p,\text{glass}}$ and the equilibrium state $C_{p,\text{vib}}$ without changing the temperature. The isothermal annealing performed here converts the nonequilibrium state of poly(styrene) glass to the equilibrium state of its liquid at a fixed T and thus only the effect of change in the structure is observed. We have already described here that on cooling from 393 to 363 K at 60 K/h rate, poly(styrene) forms its glassy state. When it is annealed for 67 ks at 363 K, it becomes an equilibrium state melt and its T_f becomes the same as its T of 363 K, while its C'_p at 3.3 mHz frequency decreases to a constant value as seen in Fig. 2. The decrease is mainly from the increase in τ_{cal} with marginally small effects from other sources listed in Eq. (1). Evidently, annealing brought the (nonequilibrium) state of a glass to the equilibrium state of a liquid as τ_{cal} increased. With an increase in τ_{cal} , its C'_p for $(\omega\tau_{\text{cal}})^2 \gg 1$ decreased mainly because of the decrease in the configurational part associated with the faster modes of the calorimetric relaxation-time distribution. The total decrease in C'_p is relatively small and this means that there is no great change in $C_{p,\text{vib}}$ on annealing a glass.

The decrease in $C_{p,\text{vib}}$ and $C_{p,\text{conf}}$ on annealing requires interpretation in terms of structural change alone at a fixed thermal energy. Its interpretation in terms of Goldstein's potential energy landscape paradigm¹⁻⁴ requires that a liquid's

state point moves on the surface of the landscape with continuously decreasing volume at a fixed thermal energy. An interpretation in the Donth *et al.*³¹ spatio-temporal density pattern fluctuations requires knowledge of the change in these fluctuations with decreasing volume at a fixed T . During the equilibration process on annealing, these fluctuations become slower with no big change in the vibrational contributions.

D. Frequency-dependent elastic constants and specific heats

Finally, we consider our results in view of the recent argument^{37,38} that certain experiments do not measure the true frequency-dependent value of C_p because (i) thermal-expansion coefficient of a liquid is finite and (ii) mechanical stress relaxes at the same time scale as the enthalpy. Instead, one measures a combination of frequency-dependent C_p and of the isochoric specific heat C_V . Christensen *et al.*³⁷ provided a one-dimensional solution to the consequent thermoviscoelastic problem for heat propagation in a planar configuration and deduced³⁷ that (i) for specific heat measurements at high frequencies or low T , the term $(C_p - C_V)/C_p$ is negligible and therefore C_p is equal to the “longitudinal specific heat” C_l , and (ii) for measurements at low frequencies and high T , the ratio of the shear modulus G to longitudinal modulus M_T , i.e., the term G/M_T is small and therefore C_p is also equal to C_l . (At $T > T_g$ or at low frequencies, G is zero for liquids, but this is not the case for most polymers in the rubber state at $T > T_g$.) Most importantly, C_p and C_l are not equal at intermediate frequencies or in the liquid’s vitrification temperature range. Also C_l itself is frequency dependent.³⁷

By using similar arguments for a sample’s spherically symmetric geometry with the heat source at the center, Christensen and Dyrre³⁸ deduced that when the liquid shell is thin, C_l is measured, but as the shell becomes thicker, C_p is measured. In this context, C_l is given by³⁸

$$C_l = \frac{3K_T}{3K_T + 4G}C_p + \frac{4G}{3K_T + 4G}C_V = \frac{K_T}{M_T}C_p + \frac{4G}{3M_T}C_V, \quad (3)$$

where K_T is the bulk modulus and $M_T = K_T + (4G/3)$. There are further relations between C_l , C_V , C_p , and adiabatic modulus.³⁹

We need to consider three consequences of Christensen *et al.*^{37,38} analysis of the thermoviscoelastic effect. First, it makes molecular interpretation of Eq. (3) somewhat difficult because the elastic constants and C_p and C_V of the equilibrium liquid vary with the measurement frequency, and these same quantities measured for the glassy state depend upon thermal history as noted already.³⁷ Second, if the quantity measured becomes a combination of C_p and C_V , it would make it difficult to interpret the enthalpy and entropy determined from the integrals of the measured specific heat.

The third consequence is for the analysis of the spectra of the *measured* real and imaginary components of the specific heat and of the plots of their fixed frequency value against T . These components would be seen as a combination of the frequency-dependent K_T , M_T , G , C_p , and C_V at a fixed T , and each of these properties would have its own characteristic

relaxation time, magnitude, and the distributions parameter. This would complicate the shape of the relaxation spectra of the measured specific heat except for certain combinations of the magnitudes, the frequency dependences, and the relaxation time distributions of K_T , M_T , G , C_p , and C_V : an aspect that needs to be formally discussed. Nevertheless, it is worth pointing out that a stretched exponential relaxation function of the type used in dielectric relaxation has been found to describe the measured C_p spectra of propylene glycol¹¹ and glycerol.⁴⁰ Moreover, the T dependence of characteristic times for K_T and for G may differ and hence the quantities K_T/M_T and G/M_T in Eq. (3) would vary nonmonotonically with T in the glass-liquid range. If the measured real and imaginary components at a fixed frequency were a combination of C_p and C_V , variation of these components with T would be more complex than that of either C_p or C_V . However, a stretched exponential relaxation function has been fitted to the plots of these components against T for molecular liquids.^{21,23} Evidently, there is a need to reconcile the fitting of this function with the arguments that only at low frequencies (or high temperatures) and high frequencies (or the glassy state)^{37,38} the measured C_p is the true C_p and at intermediate frequencies (or in the vitrification range) it is a combination of C_p and C_V . Other aspects of the sample’s volume remaining fixed or lagging in phase with the sinusoidal temperature cycle during the specific-heat measurements have been described earlier.⁴¹

When a glassy polymer is heated through its softening range, the bulk modulus decreases by a factor of 2–3, and G decreases by at least three orders of magnitude over the measurable frequency range. (Unless the terminal zone for its relaxation has been reached, G would not approach zero.) In our study, the sample consisted of less than 0.5-mm-size polystyrene granules that filled about 50% volume of the hermetically sealed capillary that was heated inward from the circumference. Even though Eq. (3) had been derived for a different sample-probe configuration, we discuss its implications^{37,38} for our findings. The quantities M_T , G , and K_T may be determined from the velocities of longitudinal and transverse waves propagation of ultrasound, V_l and V_t , and the density ρ : $M_T = \rho V_l^2$, $G = \rho V_t^2$, and $K_T = M_T - (4G/3)$. Takagi *et al.*⁴² reported the sound propagation velocity of 5 MHz frequency wave in polystyrene. We use the data at 353 K from their Fig. 3: $V_l = 2.2$ km/s and $V_t = 1.02$ km/s. Since ρ of polystyrene is 1.05 g/ml, the specific volume V is 0.952×10^{-3} m³/kg. Thus $M_T = 5.08$ GPa, $G = 1.09$ GPa, and $K_T = 3.64$ GPa, and the quantity $4G/3M_T$ in Eq. (3) is 0.286. We calculate the difference $C_p - C_V = TV\alpha^2 K_T$, where V is the specific volume or molar volume depending upon the units of C_p and C_V being used, and $\alpha [=V^{-1}(dV/dT)]$ is the coefficient of volume expansion, which is 2×10^{-4} K⁻¹ at 353 K.⁴³ The calculated difference is 0.05 J g⁻¹ K⁻¹. Thus, C_V is ~3% less than the measured C_p of ~1.5 J g⁻¹ K⁻¹. The difference $C_p - C_l [= (C_p - C_V)4G/3M_T]$ as given by Eq. (74) in Ref. 37 is 0.014 J g⁻¹ K⁻¹. This also seems negligible in comparison with the measured C_p of ~1.5 J g⁻¹ K⁻¹. Since K_T , M_T , G , C_p , and C_V in the nonequilibrium state are time dependent, C_l would depend upon the thermal history of the sample. As pointed out by Christensen *et al.*,³⁷ $C_{p,app}$ data, which are

time dependent, would also contain the above effects. The analysis shows that in our comparison of $C_{p,\text{app}}$ and C'_p , this effect would be less than 1%.

V. CONCLUSIONS

Structural relaxation of a glass on isothermal annealing decreases $C_{p,\text{conf}}$ contribution to C'_p due to (i) an increase in the average relaxation time, which bodily shifts the C'_p spectra to lower frequencies, (ii) kinetic freezing of the faster modes in the relaxation time distribution, and (iii) a decrease in the JG relaxation contribution. It also decreases the $C_{p,\text{vib}}$ contribution to C'_p due to increase in the phonon frequency

and decrease in the anharmonic force, but this decrease is negligibly small.

The unrelaxed C_p of an equilibrium melt lies on an almost linear extrapolation of the C_p against T plot of the glassy state. Therefore, almost all increase in C_p on structural un-freezing on heating a glass is configurational in origin.

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