

Vibrational and configurational parts of the specific heat at glass formation

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The specific heat C_p of a liquid is partly vibrational, arising from change in phonons and anharmonic forces with temperature T , and partly configurational, arising from change in the structure with T . The first determines a liquid's elastic resistance to stress or rigidity and the second its fluid behavior. Both are thought to decrease on liquid's vitrification, and their *ad hoc* estimates are currently used for understanding a supercooled liquid's dynamics. We report measurements of the vibrational part, $C_{p,\text{vib}}$, and determine the configurational part. It is found that there is almost no decrease in $C_{p,\text{vib}}$ on structural freezing of the polymer melts, and the decrease in C_p is configurational. An interpretation of the finding is that the curvature of the fixed configurational energy minimum in which a polymer glass structure is trapped and the associated anharmonicity have quantitatively the same effect on C_p as the corresponding two sources when its melt explores a multiplicity of high energy minima and its volume changes.

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I. INTRODUCTION

In the glassy state, molecular motions occur about an equilibrium position at the potential energy minimum and the probability of the molecules to jump to a new equilibrium position at some distance is vanishingly small. As the temperature of the glass is increased, this probability increases. In the glass-softening temperature range, it becomes high enough that Brownian diffusion becomes observable on a laboratory time scale and glass is said to become a liquid. Brownian diffusion becomes biased by an external stress and is manifested as a relaxation process or viscous flow. In the liquid state, molecules also oscillate around a mechanical equilibrium configuration at time scales of picoseconds (terahertz frequency), as in a crystalline solid, and hence a liquid in which Brownian diffusion occurs has also a solidlike rigidity, which is numerically defined by its high-frequency shear modulus. Changes in molecular dynamics during softening of a glass on heating, and in the vitrification range of a liquid on cooling, are currently of much interest, particularly in its relation to the entropy and specific heat changes. This dynamics has been discussed in terms of soft-potential models,¹⁻³ anharmonicity,⁴ and fluctuation of a liquid's thermodynamic state point in a potential energy landscape,⁵⁻⁹ the last being a description of how the energy of a system changes with the geometry of molecular arrangement, particularly with reference to structural relaxation and viscosity.¹⁻⁹

There are at least three contributions to the specific heat C_p and entropy of glass, and therefore these may not be entirely vibrational at temperature T close to its T_g . The first stems from the accepted interpretation of the nonexponential relaxation in terms of a distribution of relaxation times, which is expressed as a sum of a multiplicity of discrete relaxation processes¹⁰ or dynamic heterogeneity¹¹ with characteristic times of the processes ranging formally from a zero value to an upper limit.¹⁰ In this view, contribution to a configurational property rapidly decreases as one moves to the shorter relaxation times, and regions or entities with the

shortest relaxation time contribute the least. Thus, it has been argued^{12,13} that C_p and entropy of a glass at a temperature T immediately below T_g have a contribution from faster processes of a distribution of times and this contribution vanishes only gradually on cooling a glass.

The second contribution is from the localized motions or the Johari-Goldstein (JG) relaxation in the glassy state which have their own relaxation time distribution.¹⁴⁻²⁰ In comparison with both the vibrational part of C_p of a glass and the specific heat of the crystal state, the contribution to C_p from localized motions has also been found to be very small.^{21,22} Moreover, the localized motions' contribution to the dielectric and mechanical relaxation strengths decreases on annealing a glass,¹⁷⁻¹⁹ and it is less when a glass is formed by slowly cooling a melt.^{15,18,23,24} The third stems from anharmonic forces whose contribution rapidly decreases with the decrease in T . When the first two small contributions are ignored, C_p of a glass has mostly a vibrational component and C_p of a liquid has two components: (i) vibrational, arising from change in the force constants and frequency as different energy levels are occupied with changing T within the unchanging distribution of the available characteristic frequencies, and (ii) configurational, arising from change in the number of arrangements with changing T that the structure of liquid explores. Both contributions change on cooling until the supercooled liquid vitrifies. Thereafter, C_p of the glass has mostly a vibrational contribution $C_{p,\text{vib}}$. On heating through its softening temperature T_g , this C_p begins to gain the configurational contribution in a time- and temperature-dependent manner, reaching the full value in the ultraviscous state. Both the vibrational and configurational parts of an equilibrium ultraviscous state's C_p and entropy vary with T . The vibrational part is determined by the shape of the potential function, curvature of its minima, and anharmonic forces of the explored configurational energy minima. The configurational part is determined by the number of molecular arrangements or the configurational energy minima that a liquid of a fixed energy and volume can explore. (In contrast, an ordered crystal without point defects has only one configuration and the shape of its potential function alone deter-

mines its $C_{p,\text{vib}}$.) These concepts are at the basis of the potential energy landscape description of liquids and disordered solids. During the last decade, a number of groups^{1–9} have provided computer simulations of the thermodynamic behavior of supercooled liquids and glasses. The viscosity of a liquid has been related to its configurational entropy, which is determined from the integral $C_{p,\text{conf}} d \ln T$, where $C_{p,\text{conf}}$ is the configurational part of C_p .

Thermodynamic properties of a glass should be derivable from the vibrational partition function, and that of a liquid by configurational and vibrational partition functions. Experimentally, these have been difficult to determine and therefore *ad hoc* approximations have been made to estimate $C_{p,\text{conf}}$ for the purpose of testing the merits of the entropy-based theory of glass formation. It was recently proposed²⁵ that $C_{p,\text{vib}}$ of a metastable equilibrium liquid may be determined from specific heat spectroscopy or dynamic C_p measurements. The premise is that in measurements of the complex specific heat $C_p^* [=C_p' - iC_p'']$, where C_p' is the real and C_p'' the imaginary component and $i = (-1)^{1/2}$ as a function of frequency at a fixed T , the limiting high-frequency C_p' is the unrelaxed value, $C_{p,\infty}$, which in turn is equal to $C_{p,\text{vib}}$. To determine $C_{p,\infty}$ or $C_{p,\text{vib}}$, it is required that ω_{mod} , the temperature-modulation frequency used for measuring C_p^* of an equilibrium state, be high enough that $(\omega_{\text{mod}}\tau_{\text{cal}})^2$ in the formal equation for relaxation²⁶ of C_p' and C_p'' is much greater than 1, i.e., $C_p'' \rightarrow 0$. Here, τ_{cal} is the characteristic relaxation time of configurational enthalpy, which is mechanically and numerically different from other relaxation times. Alternatively, one may determine C_p^* as a function of T at a fixed ω_{mod} and find a temperature range over which τ_{cal} in the equilibrium liquid state is such that $(\omega_{\text{mod}}\tau_{\text{cal}})^2 \gg 1$. If $C_{p,\infty}$ of a liquid is to be determined at a higher temperature and its τ_{cal} is low, a higher value of ω_{mod} needs to be used. It should also be stressed that the liquid must remain at its equilibrium density and it should “vitrify” because its τ_{cal} is greater than the reciprocal of ω_{mod} and not because the liquid’s cooling rate is relatively rapid. This requirements ensures that C_p' has decreased to a value undetectably close to $C_{p,\infty}$ at that ω_{mod} . Experiments in which the cooling and heating rates are such that this requirement is not satisfied, the true (time-independent) C_p' would lie midway between the C_p' against the T plot measured during the heating and the cooling.

In an earlier study,²⁵ data on C_p' and $C_{p,\text{app}}$ of ultraviscous $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and $0.4\text{Ca}(\text{NO}_3)_2 \cdot 0.6\text{KNO}_3$ melts were used for this analysis,²⁵ and it was found that $C_{p,\text{vib}}$ of the equilibrium liquid at $T > T_g$ and C_p of a glass differ by an insignificant amount, and $C_{p,\text{vib}}$ lies on a linearly extrapolated line of $C_{p,\text{glass}}$.²⁵ Here, we report a fixed frequency study of C_p of four linear chain polymers and use the above-described method as a premise to determine $C_{p,\text{vib}}$ and hence $C_{p,\text{conf}}$. ($C_{p,\text{vib}}$ and $C_{p,\text{conf}}$, if coupled, would both change with T and their values are not readily separated.) It is found that the change in $C_{p,\text{vib}}$ as a glass softens on heating and becomes an ultraviscous liquid is negligibly small. This is interpreted in terms of the potential energy landscape model for structural fluctuations.

II. EXPERIMENTAL METHODS

Poly(styrene) of molecular weight of 212 400, poly(methyl methacrylate) of molecular weight of 996 000, and po-

ly(butyl methacrylate) of molecular weight of 200 000 were purchased from Aldrich Chemicals and used as such. The linear chain polymers were received as fine powder, which was transferred to a 2.2 mm internal diameter, 90 mm long, and 0.3 mm thick wall glass capillary closed at one end and accurately weighed. The amount studied was nominally 100 mg. The capillary sample holder was hermetically sealed by fusing its open end with a directed thin flame. The polymer labeled CHA-DGEBA was made by condensation polymerization of a homogeneous mixture of equimolar (stoichiometric) amounts of cyclohexylamine (CHA) and diglycidyl ether of bisphenol A (DGEBA). Cyclohexylamine of 99.5% purity was purchased from Aldrich Chemicals and DGEBA was an electronic grade material supplied by Shell Chemicals. The samples were made by accurately weighing CHA and DGEBA in equimolar ratio, mixing it in a separate container, and then transferring nominally 180 mg of the liquid in the glass capillary, which was then sealed by a thin flame. This operation took ~ 3 min. The hermetically sealed sample was heated and cooled between 300 and 393 K several times to achieve complete polymerization by condensation reaction of CHA with DGEBA in the liquid state. Other polymers in the sealed capillary were similarly thermally cycled from $T < T_g$ to $T > T_g$ in order to reduce any mechanical stresses.

The calorimeter used for the study has been described earlier.²⁷ It is designed such that the calorimetric cell is surrounded by a thermal shield which ensures a spatial distribution of the temperature along the 90 mm length of the sample holder within ± 0.05 K of the average temperature measured by the thermal sensors which are distributed along the entire surface of the cell. This calorimeter has been used earlier to study denaturation of lysozyme²⁸ and most recently to study endothermic freezing and exothermic melting of a mixture of 4-methylpyridine, α -cyclodextrin and water,²⁹ and calorimetric relaxation time of acetaminophen.²⁶ It has been used for measurements in both the adiabatic mode and temperature scanning mode, but it was used here only with temperature modulation in the scanning mode. Thus, C_p^* was measured at different temperatures during both the cooling of the sample and heating. The instrument was calibrated by using dodecane as a standard and absolute C_p values were determined. Measurements made with different samples showed a reproducibility of better than 0.5% for C_p and 100 μW for dH/dt .

The sample holder containing the polymer was inserted into the calorimeter cell maintained at a suitable temperature and allowed to come to a constant temperature, as given in the figure captions. The sample was cooled or heated at a fixed rate q of 12 K/h, which is 1/50th of the rate of 10 K/min (600 K/h) normally used in differential scanning calorimetry (DSC) studies. These rates are comparable to the usual adiabatic calorimetry experiments. The sinusoidal peak to peak modulation temperature was 1 K and the modulation frequency was 20.95 mrad/s (3.33 mHz or oscillation period of 300 s). This temperature modulation was superposed on the cooling and heating ramps. The temperature of this ramp, averaged over each cycle, is taken as the measurement temperature T here.

It should be stressed that the duration of each experiment in this study was about 5–6 h for cooling, and for heating

with 30 min wait before cooling and before heating; thus, a total period of 10–12 h was taken for C_p^* measurements in one thermal cycle. The long duration experiments performed here also required greater sensitivity and thermal stability, which was an advantage of this calorimeter. In contrast, the usual DSC studies take 8–10 min for 10 K/min rate scans and about 80–100 min for 1 K/min heating rate.

III. RESULTS

Briefly, temperature-modulated scanning calorimetry (TMSC) measurements yield both C_p' and C_p'' and the time- and structure-dependent nonequilibrium specific heat $C_{p,app}$ as in the usual DSC and adiabatic calorimetry experiments simultaneously for the same temperature and time conditions.^{30–34} In the $C_{p,app}$ measurements, any heat released or absorbed irreversibly during the heating and cooling is also measured. Analysis of the quantities C_p' , C_p'' , and $C_{p,app}$ with model fitting yields the relaxation time, the relaxation time distribution, and the structure-dependent parameters. Since our study is concerned with the specific heat change with temperature T and analysis for $C_{p,vib}$ and $C_{p,conf}$, only C_p' and $C_{p,app}$ measured during the cooling and subsequent heating of the samples at 12 K/h (0.2 K/min) rate are reported. Figure 1(a) shows the C_p' and $C_{p,app}$ plots for poly(styrene) and Fig. 1(b) shows the enlargement of the plots in the structural freezing and unfreezing temperature range. Figures 2(a) and 2(b) show the corresponding plots for poly(methyl methacrylate), Figs. 3(a) and 3(b) those for poly(butyl acrylate), and Figs. 4(a) and 4(b) those for the CHA-DGEBA polymer.

The onset temperature at which $C_{p,app}$ begins to decrease for cooling, $T_{onset,cool}$, was determined from the intersection of two straight lines in Fig. 1(a), one is a tangent drawn from the inflexion point and the other is a linear extrapolation of $C_{p,0}$ to lower temperatures. It is indicated by a downward arrow in Figs. 1–4 and its value for the four polymers is listed in Table I. The onset temperature for $C_{p,app}$'s sigmoid shape rise was also determined by drawing a tangent to the inflexion point and extending the $C_{p,app}$ from the glassy state to the melt or rubber state of the polymers. (Note that this T_{onset} is distinguished from the usual T_g that is determined by heating at 10 or 20 K/min rate.) Its value and that of $C_{p,app}(T_{onset})$ and $C_p'(T_{onset})$ during heating are listed in Table I, where the temperature at which $C_{p,app}$ shows a peak, T_{peak} , is also listed.

It is worth noting that there is a characteristic difference between mechanical and dielectric relaxation measurements and the temperature-modulated calorimetry. In the mechanical and dielectric relaxation measurements, the oscillating stress or electric field has no effect on the equilibrium properties. In contrast, modulation of a material's temperature in TMSC experiments has an effect on $C_{p,0}$ and $C_{p,\infty}$ as well as on τ_{cal} and the diffusion coefficient. Since these quantities vary with T , $C_{p,0}$, $C_{p,\infty}$, and τ_{cal} do not vary with the same mean temperature as the mean (sinusoidal) modulation temperature. This effect, which is relatively small and negligible because the modulation amplitude is small, has been formulated and its consequences have been discussed.^{35,36}

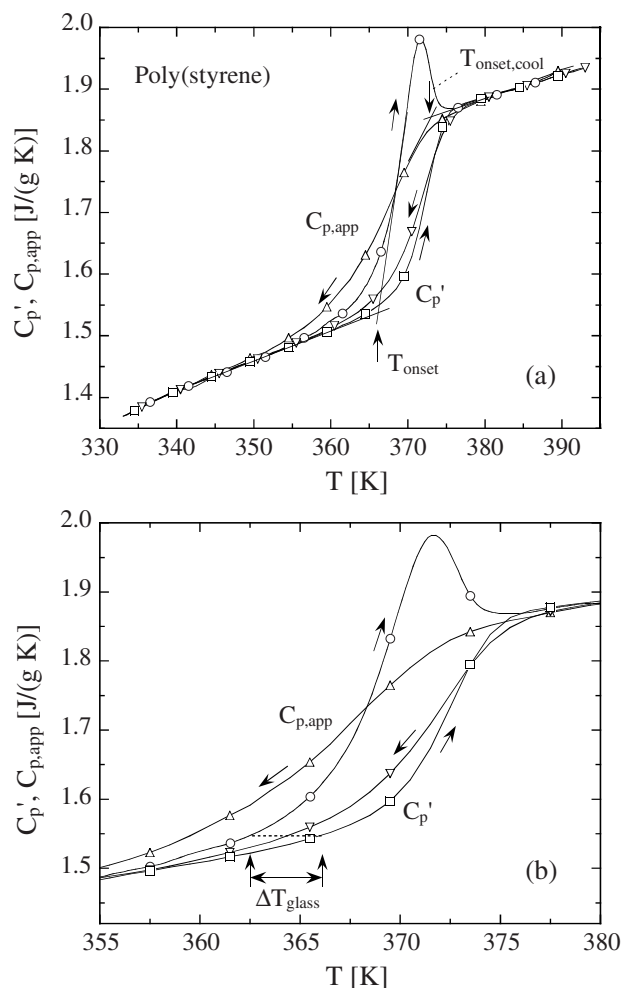


FIG. 1. (a) The C_p' and $C_{p,app}$ for poly(styrene) measured at 20.95 mrad/s frequency by heating and cooling at 12 K/h is plotted against the temperature. The sample was kept for 0.5 h at 393 K, cooled to 333 K, kept for 0.5 h at 333 K, and then heated to 393 K. (b) Enlargement of the plots in the structural freezing (unfreezing) range. For clarity, only one in five data points collected is shown in (a) and only one in four in (b). Normal triangles are for the $C_{p,app}$ measured during the cooling and circles for those measured during the heating. Upside down triangles are for C_p' measured during cooling and squares for those measured during the heating.

IV. DISCUSSION

First, we briefly describe how specific heat spectroscopy developed by Birge and Nagle^{37,38} can be used to determine the $C_{p,vib}$ and $C_{p,conf}$ and related quantities. The technique yields $C_{p,\infty}$, $C_{p,0}$, the distribution of relaxation time parameter β , and τ_{cal} at a fixed T from one spectra, and Menon³⁹ has used it to determine these quantities for di-*n*-butylphthalate at different T . Alternatively, one may keep ω_{mod} fixed and determine these quantities by measuring the real and imaginary components of the complex specific heat over a broad temperature range. Since $C_{p,\infty}$ is the unrelaxed C_p , its measured value is not affected by the increase in τ_{cal} as long as the $(\omega_{mod}\tau_{cal})^2 \gg 1$ condition is satisfied, as noted in the study of acetaminophen.²⁶ In the latter case, the mid-

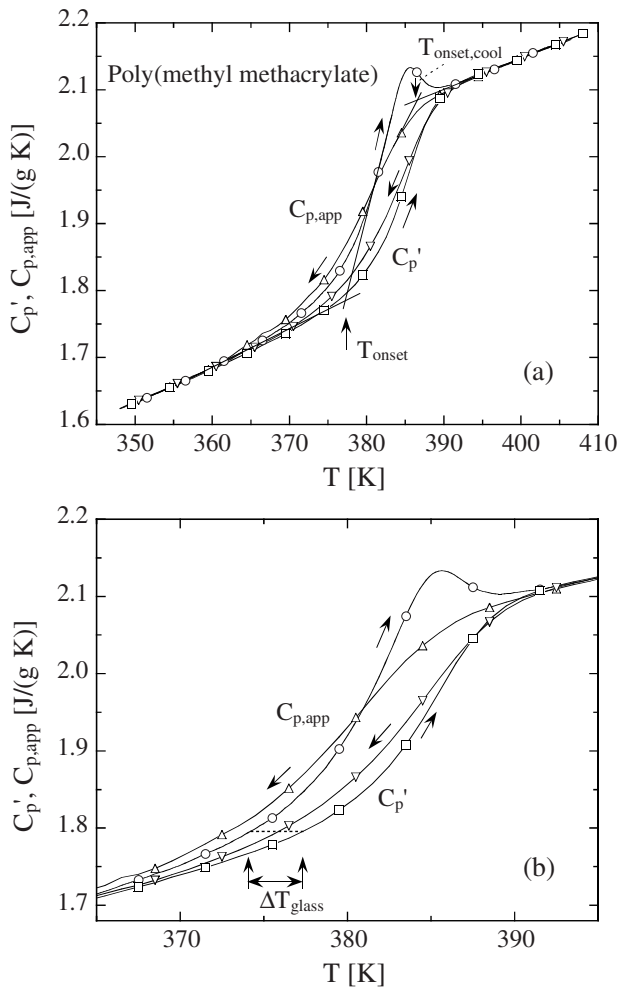


FIG. 2. (a) The C_p' and $C_{p,app}$ for poly(methyl methacrylate) measured at 3.33 mHz frequency by heating and cooling at 12 K/h is plotted against the temperature. The sample was kept for 0.5 h at 408 K, cooled to 348 K, kept for 0.5 h at 348 K, and then heated to 408 K. (b) Enlargement of the plots in the structural freezing (unfreezing) range. For clarity, only one in five data points collected is shown in (a) and only one in four in (b). For clarity, only one in five data points collected is shown in (a) and only one in four in (b). Normal triangles are for the $C_{p,app}$ measured during the cooling and circles for those measured during the heating. Upside down triangles are for C_p' measured during cooling and squares for those measured during the heating.

point or the inflexion point of the C_p' plots against T yields the temperature at which τ_{cal} is equal to the inverse of ω_{mod} . In contrast, $C_{p,app}$ measurements yield T_g on heating as well as the onset temperature of structure freezing on cooling $T_{onset,cool}$ but not τ_{cal} , which can be obtained by model fitting or else approximated. When $C_{p,app}$ is determined from a DSC scan by heating at 20 K/min rate, the onset temperature of the sigmoid shape rise in $C_{p,app}$ is defined as T_g and τ_{cal} estimated at this T_g is ~ 50 s. This τ_{cal} corresponds to the value at the inflexion temperature of the sigmoid shape C_p' increase in Figs. 1–4 for the equilibrium condition, i.e., when C_p' for ω_{mod} of 20.95 mrad/s is the same for heating and cooling at a very slow rate. When $C_{p,app}$ is measured during heating at still slower rate, the sigmoid shape $C_{p,app}$ rise

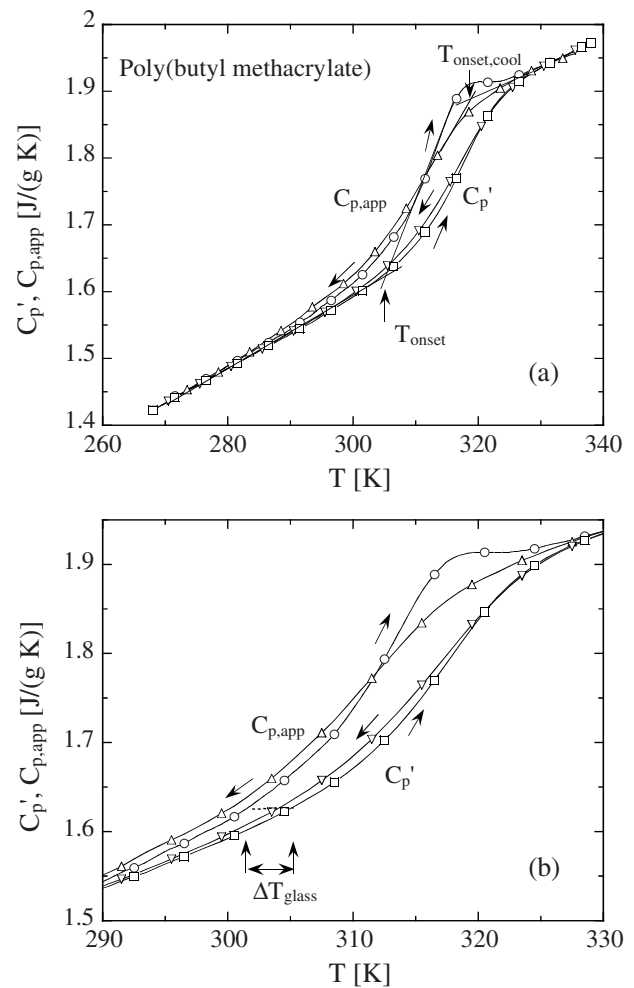


FIG. 3. (a) The C_p' and $C_{p,app}$ for poly(butyl methacrylate) measured at 3.33 mHz frequency by heating and cooling at 12 K/h is plotted against the temperature. The sample was kept for 0.5 h at 338 K, cooled to 268 K, kept for 0.5 h at 268 K, and then heated to 338 K. (b) Enlargement of the plots in the structural freezing (unfreezing) range. For clarity, only one in five data points collected is shown in (a) and only one in four in (b). Normal triangles are for the $C_{p,app}$ measured during the cooling and circles for those measured during the heating. Upside down triangles are for C_p' measured during cooling and squares for those measured during the heating.

would shift to lower T and T_{onset} would be lower and τ_{cal} longer. For the low heating rate of 12 K/h in this study, the $C_{p,app}$ against T plots are therefore found to be shifted to lower T range and T_{onset} is less than the midpoint temperature of the C_p' against the T plot. The T_{onset} of the $C_{p,app}$ against the T plot for 20 K/min rate would be at the inflexion temperature of the C_p' plot for ω_{mod} of 20.9 mrad/s.

The shape and the position of the C_p' plots in the T plane also vary with the cooling and heating rates. During measurements at a fixed ω_{mod} performed during cooling and heating at a high rate, structural relaxation occurs at different rates, C_p' measured during cooling and heating differ, and their plots against T do not superpose. In Figs. 1–4, C_p' measured during cooling is lower for all polymers than that measured during heating at high temperatures and is higher at

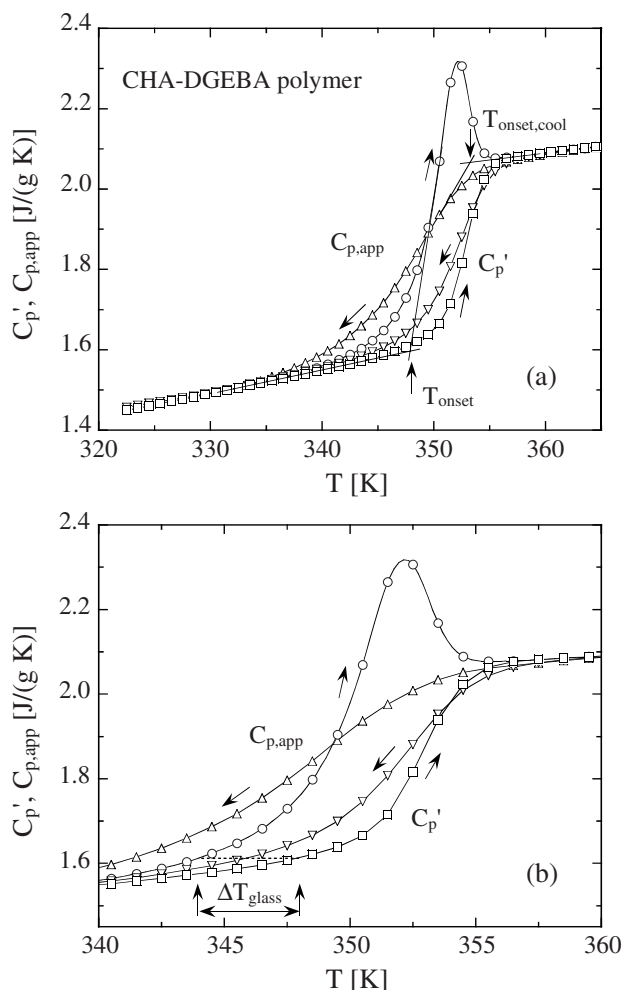


FIG. 4. (a) The C_p' and $C_{p,app}$ for CHA-DGEBA (molar ratio 1:1) measured at 3.33 MHz frequency by heating and cooling at 12 K/h is plotted against the temperature. The sample was kept for 0.5 h at 382 K, cooled to 322 K, kept for 0.5 h at 322 K, and then heated to 382 K. (b) Enlargement of the plots in the structural freezing (unfreezing) range. All data points collected are shown. Normal triangles are for the $C_{p,app}$ measured during the cooling and circles for those measured during the heating. Upside down triangles are for C_p' measured during cooling and squares for those measured during the heating.

low temperatures. If the state of the polymer remained at equilibrium, C_p' measured during the cooling would be the same as that measured during the heating at the same rate.

We have also found that when the heating and cooling rates q are decreased, C_p' at a fixed T increases. Also, in general, when q is decreased, the C_p' -cooling and C_p' -heating curves shift toward each other and ultimately merge at the median. When the two curves have merged, the equilibrium state is maintained during measurements on cooling and heating and for such conditions, $C_{p,\infty}$ or the unrelaxed value of C_p' of an equilibrium liquid may be determined.

To demonstrate this occurrence, an enlargement of the plots of C_p' of poly(vinyl acetate) of molecular weight of 184 000 measured during cooling and heating at 24, 12, and 8 K/h rates and also on cooling at 0.5 K/h rate is shown in Fig. 5. It is evident that C_p' measured during the cooling and

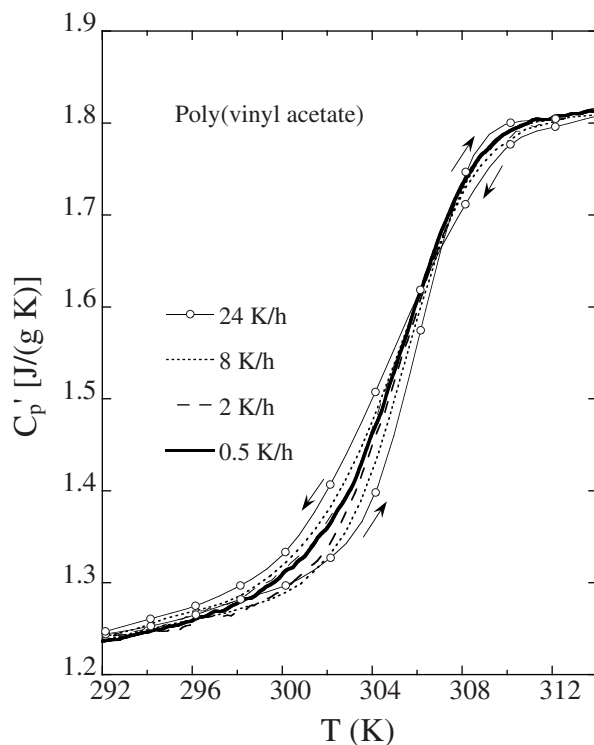


FIG. 5. Enlargement of the plots of C_p' against the temperature, measured at 20.95 mrad/s frequency during cooling and then heating poly(vinyl acetate) at rates q of 24, 8, and 2 K/h. The continuous line is for C_p' measured during cooling at 0.5 K/h. As q is decreased, the C_p' plots for cooling and heating approach each other and tend to superpose. This yields the criterion that the material is in an equilibrium state when C_p' is the same for cooling and heating. This would be the case for q of 0.5 K/h cooling of poly(vinyl acetate), as the plot shown by thick line lies at the median of the other plots.

heating approach each other and tend to merge at the median value. This value would be indistinguishable from the continuous heavy line for C_p' measured during cooling at 0.5 K/h rate. Dynamic specific heat study of ultraviscous acetaminophen has also shown that C_p' measured during the cooling and heating at the low rate of 1 K/h are the same.²⁶ We use the known criterion²⁶ that C_p' measured during cooling and during heating show a large hysteresis when the cooling rate is fast and this hysteresis vanishes and the values for two experiments approach a median value when the cooling and heating rates are decreased. This median value corresponds to the equilibrium state of a polymer. Therefore, when C_p' at the lowest cooling and heating rates are not available, C_p' of the equilibrium melt would lie approximately at the median of the two C_p' against T plots measured during the cooling and heating. In the temperature range over which C_p' are the same during such a slow cooling and heating, $T_{onset,cool}$ would be relatively much less.

The high temperature limiting value of C_p' agrees with $C_{p,app}$ for all cooling and heating rates in Figs. 1–4. Here, they are equal to the relaxed specific heat $C_{p,0}$ of the polymers, which is the sum of $C_{p,conf}$ the contribution from the accessibility of different configurations to the polymer

TABLE I. The relaxation properties of four polymers from measurements of $C_{p,\text{app}}$ and C'_p during the cooling and heating at 12 K/h rates. C'_p was measured for temperature modulation frequency of 20.95 mrad/s. $T_{\text{onset,cool}}$ is the onset temperature for structural freezing, T_{peak} is the overshoot peak temperature, T_{onset} the onset temperature of sigmoid shape $C_{p,\text{app}}$ rise on heating, and $C_{p,\text{app}}(T_{\text{onset}})$ and $C'_p(T_{\text{onset}})$ are, respectively, $C_{p,\text{app}}$ and C'_p at T_{onset} . Finally, $T[C_{p,\text{app}}=C'_p(T_{\text{onset}})]$ is the temperature at which $C_{p,\text{app}}$ reaches the same value as $C'_p(T_{\text{onset}})$. $\Delta T_{\text{glass}}=T_{\text{onset}}$ minus $T[C_{p,\text{app}}=C'_p(T_{\text{onset}})]$.

Polymer	$T_{\text{onset,cool}}$ (K)	T_{peak} (K)	T_{onset} (K)	$C_{p,\text{app}}(T_{\text{onset}})$ (J/g K)	$C'_p(T_{\text{onset}})$ (J/g K)	$T[C_{p,\text{app}}=C'_p(T_{\text{onset}})]$ (K)	ΔT_{glass} (K)
Poly(styrene)	372.8	371.5	366.1	1.62	1.55	362.5	3.6
Poly(methyl methacrylate)	386.3	385.4	377.3	1.85	1.80	374.1	3.2
Poly(butyl methacrylate)	318.7	320.3	305.1	1.66	1.63	301.4	3.7
CHA-DGEBA polymer	353.2	352.2	348.0	1.76	1.65	343.9	4.1

chains, and $C_{p,\text{vib}}$, the contribution from phonons and the associated anharmonic forces. In the glassy state at low temperatures, C'_p measured during the cooling agrees with that measured during the heating in Figs. 1–4. Similarly, $C_{p,\text{app}}$ agree. At $T=T_{\text{onset}}$, $C_{p,\text{app}}$ listed in Table I is slightly higher than C'_p and $dC_{p,\text{app}}/dT$ is also higher than dC'_p/dT . This indicates that $C_{p,\text{app}}$ contains further contributions from two sources; (i) the kinetically unfrozen, faster modes in the distribution of relaxation times of the viscosity-determining α process^{12,13} and (ii) the localized motion of the JG relaxation,^{19,20} which has been observed in both the rigid structure of a glass and in ultraviscous liquids by dielectric and mechanical relaxation spectroscopy.^{14–20} Both features have been known to contribute to C_p and entropy of a glass.^{12,13} Their contributions to $C_{p,\text{app}}$ and C'_p decrease when the glass is made by slow cooling of the liquid, as is the case here, and/or the glass has been annealed to lower its fictive temperature, T_f , as both procedures serve to lower T_f of a glass.^{40,41} Because of that, the low-temperature $C_{p,\text{app}}$ values in Figs. 1–4 are closer to the $C_{p,\infty}$ or unrelaxed C_p , and therefore they would be equal to $C_{p,\text{vib}}$.

Finally, we compare $C_{p,\text{app}}$ of the glassy state of polymers against $C_{p,\text{vib}}$ determined from the plots of C'_p . To do so, we determine the equilibrium state C'_p value at T_{onset} given in Table I and list it as $C'_p(T_{\text{onset}})$ also in Table I. We then determine the temperature at which $C_{p,\text{app}}$ is the same as $C'_p(T_{\text{onset}})$. This temperature is denoted as $T[C_{p,\text{app}}=C'_p(T_{\text{onset}})]$ and listed in Table I. The difference between this temperature and T_{onset} is denoted as ΔT_{glass} in Table I. It is 3.6 K for poly(styrene), 3.2 K for poly(methyl methacrylate), 3.7 K for poly(butyl methacrylate), and 4.1 K for the CHA-DGEBA polymer. This shows that $C_{p,\text{vib}}$ at $T < T_{\text{onset}}$ for the polymers is the same as $C_{p,\text{vib}}$ at $T \geq T_{\text{onset}}$, with the temperature differing by 3.2–4.1 K.

At a temperature of ΔT_{glass} below T_{onset} , the polymers are deep in the glassy state and their $C_{p,\text{app}}$ would be the $C_{p,\text{vib}}$ of their glassy state at that temperature. This equality also shows that there is no increase in $C_{p,\text{vib}}$ when the polymer structure unfreezes on heating. Since the unrelaxed C'_p of an equilibrium liquid can not be less than $C_{p,\text{vib}}$ of a glass, we conclude that part of the difference ($C_{p,\text{app}} - C'_p$) is due to the contribution to $C_{p,\text{app}}$ from the faster modes in the distribution of α -relaxation times and the JG relaxation.^{12,13} These contributions are reduced when T_{onset} is decreased by slower heating and T_f decreases.

In Goldstein's⁵ potential energy landscape description,^{5–9} each configurational state is associated with a minimum of potential energy in the configurational space of the system. Thermodynamic properties are derivable from the knowledge of vibrational and configurational partition functions. Specific heat increases in a sigmoid shape manner when a glass structure kinetically unfreezes on heating and becomes free from its single configurational state, but the kinetically unfrozen liquid explores many configurational states over time. As the temperature is further increased, the configurational states explored by the liquid are of higher energy. In the configurational entropy theory, the vibrational partition function and hence C_p are assumed to be insensitive to the configurational minima the liquid explores whatever its potential energy. This implies that there are more minima of high energy than of low energy in the configurational space, and thus exploring the minima is driven by entropy and not by energy.²¹ It has also been deduced²¹ that configurational states of higher energy explored by the liquid may be associated with lower vibrational frequencies and/or greater anharmonicity, which means that $C_{p,\text{vib}}$ of the liquid increases as T increases.

The continuous increase or lack of appreciable change in $C_{p,\text{vib}}$ on structural unfreezing observed here does not support the calculation-based finding that $C_{p,\text{vib}}$ is 13%–58% of the net C_p increase at the glass-liquid transition of different polymers.⁴² In terms of the potential energy landscape, it means that as the liquid begins to explore configurational minima of different energies, the curvature of the minima that determines $C_{p,\text{vib}}$ through the vibrational frequencies and the associated anharmonic contributions does not change appreciably from those in the glassy state. More likely, the net effect of the curvature of the minimum in which a glass configuration is trapped and the associated anharmonic contributions to $C_{p,\text{vib}}$ is about the same as the net effect of the same sources to $C_{p,\text{vib}}$ when an equilibrium liquid explores a multiplicity of high energy minima at T not far above T_g .

We now discuss the consequences of our findings for the entropy's relation with the mechanical relaxation of polymers⁴³ and viscosity^{44–46} of molecular liquids. In this discussion, the mechanical relaxation time, viscosity, and τ_{cal} vary as $\exp(C/TS_{\text{conf}})$, where C is a material-characteristic constant and S_{conf} is the configurational entropy. It is determined from the integral of $C_{p,\text{conf}} d \ln T$ plus the residual entropy at 0 K, where $C_{p,\text{conf}}=C_p - C_{p,\text{vib}}$. A test for the merits

of this theory therefore requires knowledge of $C_{p,vib}$. As $C_{p,vib}$ could not be determined by experiments in earlier studies, *ad hoc* approximations have been made to estimate its value for testing the merits of the Adam-Gibbs configurational entropy theory⁴⁷ by using the change in the dielectric relaxation time with temperature and/or with pressure,^{48–50} and merits of such $C_{p,vib}$ and S_{conf} estimates have been questioned.^{51–54} Following Goldstein's^{21,55} discussion of the possibility that the decrease in C_p observed on the glass formation may be partly due to the decrease in $C_{p,vib}$ and mostly due to loss of a liquid's structural fluctuation on kinetic freezing on the laboratory time scale, DiMarzio and Dowell⁴² incorporated the change in lattice vibrations in the configurational entropy theory for polymers^{44–46} and concluded that there are three parts to the equilibrium value of C_p . The net configurational part arising from the shape change of the molecules and volume expansion on heating is $\sim 80\%$ of ΔC_p , the total C_p change at the glass-softening temperature T_g , and there is a vibrational contribution of $\sim 20\%$ arising from change in the phonon frequency or the force constants. This contribution varies for different polymers and is in the range of 13% for poly(isobutylene) to 58% for poly(propylene oxide). Experimental determination of $C_{p,vib}$ change at T_g suggests a need for reconsidering these calculations. From the analysis of the specific heat data,^{12,21,22,55} it had been concluded that in addition to the vibrational part, C_p of a glass at T close to the calorimetric T_g contains contributions from localized molecular motions that show up as secondary (β or the Johari-Goldstein) relaxations and part from anharmonic forces. These two contributions are relatively small. Moreover, it has been found that the strength of the dielectrically and mechanically observed secondary relaxation rapidly decreases when T_f of a glass is decreased either by annealing it^{17,23,24} or by producing it by slowly cooling the melt.^{14,15,18,19,56} Therefore, the contribution from secondary relaxation should be negligible in the sample vitrified by slow cooling here. More recently, it has

been reported⁵⁷ that the Adam-Gibbs equation empirically fits the data for polymers if it is assumed that secondary relaxation makes a 50%–90% contribution to the total excess entropy at T_g , via a very large contribution to C_p from the secondary relaxation in polymers. However, there is no independent information for such a large magnitude for such a contribution in a rigid glass or liquid and the fitting seems to be due to a multiplicity of approximations made.

V. CONCLUSIONS

Dynamic specific heat measurements of four linear chain polymers show that (i) the unrelaxed C'_p in the equilibrium state is the same as the vibrational specific heat of the glassy state, (ii) at T_{onset} , $C_{p,app}$ is higher than C'_p or $C_{p,vib}$, and (iii) the unrelaxed C'_p at $T \geq T_{onset}$ is equal to C_p at $T < T_{onset}$. The prediction for the increase in $C_{p,vib}$ based on theoretical modification⁴² of the $C_{p,conf}$ in the entropy theory^{44–47} could not be supported. Almost all increase in C_p of polymers on heating through T_g seem configurational in origin. Lack of increase in $C_{p,vib}$ on structural unfreezing observed here means that as the liquid explores configurational minima of different energies, the curvature of the minima that determines $C_{p,vib}$, through the vibrational frequencies, and the anharmonic contributions due to its asymmetry do not change appreciably from those in the glassy state. The net effect of the curvature of the energy minima in which a glass configuration is trapped and the associated anharmonic contributions to $C_{p,vib}$ is about the same as the net effect from the same sources when a liquid explores a multiplicity of high energy minima and its volume changes with temperature.

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