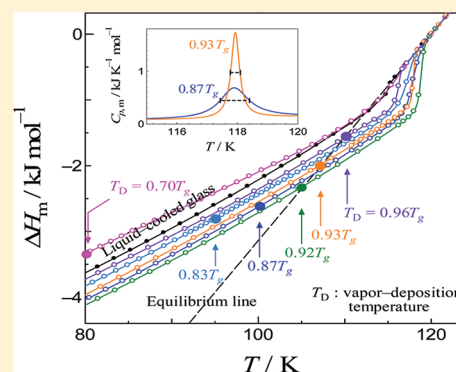


Character of Devitrification, Viewed from Enthalpic Paths, of the Vapor-Deposited Ethylbenzene Glasses

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ABSTRACT: Enthalpic path and enthalpy-relaxation rates of ethylbenzene glasses prepared by vapor deposition at various temperatures, T_D , were examined on heating intermittently with a high-precision adiabatic calorimeter. It was confirmed that when T_D is in the range $0.79\text{--}0.96T_g$, the enthalpies elucidated at their preparation temperatures, i.e., T_D , are lower than those of the liquid-cooled glass. The fictive temperature T_f at which the enthalpy path of each glass crosses the enthalpy curve expected for the equilibrium supercooled liquid was observed to be lowest when $T_D = 0.92T_g = 105\text{ K}$. The glasses revealed two remarkable characteristics: first, the temperature of the peak in the endothermic effect, which corresponds to the temperature $T_{g,\text{dev}}$ of the steepest devitrification, was observed to increase in correlation with the low-enthalpic nature of the glasses. Second, the devitrification manner was quite different between the glasses with $T_D < 0.92T_g$ and $T_D \geq 0.92T_g$, even if the two glasses have the same T_f ; the former devitrified gradually and the latter relatively sharply.



INTRODUCTION

Recently, there is much interest concerning the ability to tune the properties of vapor-deposited glasses by varying parameters such as deposition temperature T_D , deposition rate ν_D , and film thickness d .^{1–12} The dependence of the kinetic stability on deposition temperature T_D and rate ν_D was initially studied with DSC by Ediger's group on rather complex molecules, indomethacin (IMC) and tris(naphthyl)benzene (TNB).^{1,2} It was shown, by setting ν_D constant ($=15\text{ nm s}^{-1}$) and T_D in the vicinity of T_g , that $30\text{--}60\text{ }\mu\text{m}$ thick IMC glassy films could be prepared with enhanced kinetic stability, i.e., with higher devitrification-temperature $T_{g,\text{dev}}$ than the glass transition temperature T_g of the liquid-cooled glass, and that the fictive temperatures T_f of the films were correspondingly low.² The highest kinetic stability, i.e., the highest $T_{g,\text{dev}}$, was observed when $T_D = 0.85T_g$ with the lowest T_f . Investigations on the influence of ν_D on T_f with $T_D = 0.85T_g$ showed that the kinetic stability of these $30\text{--}60\text{ }\mu\text{m}$ thick films could be further increased with decreasing ν_D . Ediger's group also has clarified the properties of the devitrification of the vapor-deposited glasses by using wide-angle X-ray scattering (WAXS), secondary ion mass spectrometry, and reversing heat capacity:^{3–8} to be intriguing, it was claimed that the transformation proceeds through propagation of the growth front with a crossover between surface-initiated and bulk ones at $1\text{ }\mu\text{m}$ thick in the case of IMC.

Ishii and Nakayama among the present authors also investigated the properties of molecular films vapor-deposited in the vicinity of T_g . T_D dependence of molar volume was examined for simple alkylbenzene molecules such as toluene (TL), ethylbenzene (EB), propylbenzene (PB), and isopropylbenzene (IPB).^{9,10} These films,

which were $10\text{ }\mu\text{m}$ thick and deposited at a rate of 3.3 nm s^{-1} , became denser as T_D approached T_g from low temperatures and a molar-volume minimum was observed when $T_D = 0.9T_g$ for EB, PB, and IPB, and $T_D = 0.8T_g$ for TL. Leon-Gutierrez et al. also examined, using in situ nanocalorimetry, the stability of the TL and EB glasses vapor-deposited at rates of $0.001\text{--}0.1\text{ nm s}^{-1}$ and with $100\text{--}200\text{ nm}$ thick.^{11,12} Their result that the stability of both of the compounds is maximized in the vicinity of $T_D = 0.8T_g$ is quantitatively a little different from the result by Ishii and Nakayama. To be interesting, furthermore, it was found by Ishii and Nakayama that the density of these glasses prepared at $T_D = 0.9T_g$ was larger than that expected for an equilibrium supercooled liquid.^{9,10} This result, aligned with WAXS^{3,8} and DSC experimental results on IMC,^{4–7} has evidenced the possibility that vapor-deposition may be used to fabricate amorphous states with more densely packed molecular arrangements as compared to those glasses prepared by liquid-cooling, i.e., slowly cooling the supercooled liquid.

In view of the increasing scientific interest surrounding these kinetically stable/highly dense glasses, the need for more precise measurements to confirm the nature of these glasses becomes indispensable. For this reason, in the present study, high precision measurements on the enthalpic states and their devitrification paths of the glasses of a simple-molecular substance EB prepared by vapor-deposition at temperatures near T_g have been carried out with an adiabatic calorimeter¹³ designed for vapor-deposited samples.

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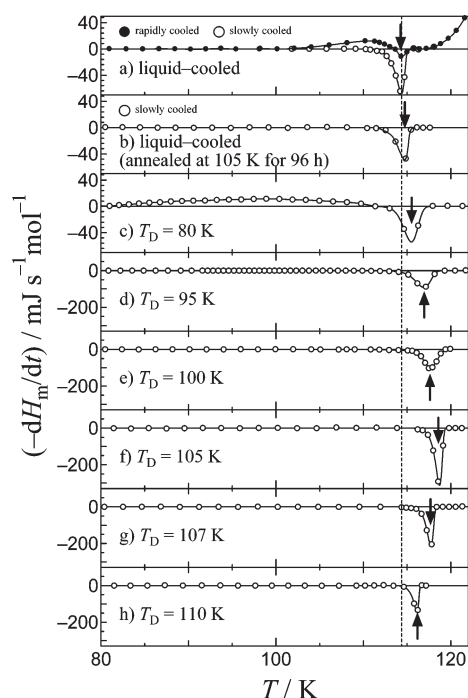


Figure 1. Temperature dependence of the spontaneous heat-release or -absorption rates observed in the intermittent heating processes under adiabatic conditions, for the glasses (c–h) prepared by vapor-deposition at different temperatures T_D , the liquid-cooled glass (a), and the liquid-cooled glass (b) with aging at 105 K for 96 h. The ordinate scales are different between the panels for glasses a–c and d–h. The arrow indicates the devitrification temperature $T_{g,dev}$ at which the endothermic effect shows its maximum.

EXPERIMENTAL SECTION

Commercial reagent ethylbenzene (EB) was purchased from Tokyo Chemical Ind. Co. Ltd. with a chemical purity of 99.0%. The reagent was purified by fractional distillation at an atmosphere prior to use. The fusion temperature of the sample was determined by the present calorimetric measurements to be (178.16 ± 0.05) K in reasonable agreement with that reported from ref 14, (178.08 ± 0.02) K.

A homemade high-precision adiabatic calorimeter of the filling-tube type¹⁵ was employed for the enthalpy increment and enthalpy-relaxation rate measurements. With this type of calorimeter, sample deposition proceeds by introducing the sample, in the vapor state, into a calorimeter cell through a filling tube. The filling tube is permanently fixed onto the cell, at one end, and is attached to a system of glass line, which allows for the collection of the vapor from the sample in the liquid state, at the other. The wall and vanes of the gold-plated copper cell act as the substrate for the vapor-deposition. During the deposition process, the cell was constantly held at a fixed temperature in order to establish the desired deposition temperature T_D . The temperature of the cell was monitored with the resistance of a Rh–Fe resistance thermometer and controlled during the sample vapor-deposition within ± 0.1 K. The base pressure within the cell, measured on the glass line system, was of the order of 10^{-3} Pa prior to deposition commencement. The pressure during deposition was not monitored as to prevent sample decomposition, thereby increasing sample impurity, expected to occur at the pressure gauge; nevertheless, a pretrial suggested that the base

pressure during deposition was kept in the range of 10^{-2} Pa. Real-time sample deposition was inferred by observing the decrease of the surface meniscus of the liquid sample contained in a thin glass cylinder. From the extent of the meniscus decrement as a function of time, the flow rate of the sample vapor was estimated. This rate was adjusted by use of a needle-valve, which joins the filling tube arising from the calorimeter cell to that evolving from the glass line system and is located just above the cryostat of the calorimeter. In the present experiments, the average deposition rates were estimated to be (2 ± 0.5) nm s⁻¹ after taking into account a fair estimation for the inner surface area of the calorimetric cell, which is the substrate area for sample deposition. The overall deposition time was on average ca. 96 h for each sample. The film's thickness was estimated to be ca. 0.5 mm. Once deposited, the sample was immediately cooled below the deposition temperature, the cryostat's inner environment was thoroughly refrigerated, and subsequently, the measurements were carried out by the intermittent heating method under adiabatic conditions; thermometry and heating procedures were repeated alternately. The amount of the sample was calculated from the molar heat capacities in the crystalline state by comparing with those found in the literature.¹⁴ By this procedure, the obtained molar heat capacity values were scattered with an error margin less than 2%, and the resultant sample amount was in agreement, in most cases, with the measured enthalpy of fusion for the crystal to within $\pm 1\%$. The average rate of heating for the measurements was ca. 40 mK min⁻¹.

RESULTS

Spontaneous Enthalpy-Relaxation Displayed by the Vapor-Deposited Glasses. Figure 1c–h shows the temperature dependence of the rates of spontaneous enthalpy-relaxation for the glasses vapor-deposited at various T_D s, and Figure 1a shows that of the liquid-cooled glasses prepared by cooling, rapidly at 10 K min⁻¹ or slowly at 10 mK min⁻¹, respectively, from 120 K, the liquid sample obtained by devitrification of the $T_D = 100$ K glass. Figure 1b shows the data for another liquid-cooled glassy sample, prepared in similar manner to that in Figure 1a, but aged at 105 K for ca. 96 h on the precooling way. Solid lines represent the curves drawn by smoothly joining the data points as a guide for the eyes. When the liquid was cooled rapidly and slowly, as seen from Figure 1a, the dependence yielded a hysteresis effect, which is characteristic of the structural relaxation in the glass transition region;¹⁶ namely, the rapidly cooled glass reveals a low-temperature exothermic ($-dH_m/dt > 0$) signal followed by a small endothermic ($-dH_m/dt < 0$) one with increasing temperature, whereas the slowly cooled glass reveals rather only an endothermic effect. The T_g has been empirically determined as the temperature at which the slowly cooled glass exhibits the maximum endothermic effect by adiabatic calorimetry; $T_{g,liq} = 114.5$ K in the present case (the subscript liq has been added to emphasize that this is the T_g value observed for a liquid-cooled glass). Notably, even when the slowly cooled glass was aged at 105 K, the observed endothermic signature (Figure 1b) resembled very much that of Figure 1a.

The temperature dependence of the rates for the glass vapor-deposited at 80 K (see Figure 1c) shows a different behavior from those observed for the liquid-cooled glasses. Essentially, a very broad exothermic effect was observed in a wide temperature range starting at 82 K slightly higher than the $T_D = 80$ K and ending at 112 K slightly lower than the $T_{g,liq} = 114.5$ K. This behavior is similar to the one reported previously for the glasses

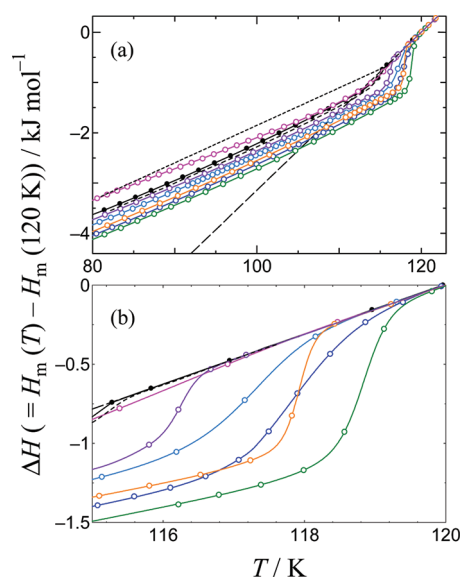


Figure 2. Enthalpy paths followed by the differently vapor-deposited and slowly liquid-cooled glasses, shown in a wide temperature range of 80–123 K (a) and on an enlarged scale in a range of 115–120 K (b): black circles, liquid-cooled glass; black short-dashed line, liquid-cooled glass with aging at 105 K for 96 h; pink circles, $T_D = 80$ K; blue circles, $T_D = 95$ K; deep blue circles, $T_D = 100$ K; green circles, $T_D = 105$ K; orange circles, $T_D = 107$ K; purple circles, $T_D = 110$ K glass. A dashed line represents the temperature dependence of the enthalpies for the supercooled liquid under equilibrium, and the dotted line is the enthalpy curve expected for the $T_D = 80$ K glass without the spontaneous heat-release or -absorption effect. Curved lines running through the circles were drawn to link the data points smoothly; a sigmoid function was used in the fitting of the step-like dependence in the devitrification range.

vapor-deposited at temperatures much below $T_{g,liq}$.^{15,17,18} Contrary to the behavior for the $T_D = 80$ K glass, however, the dependence of the rates observed for the glasses deposited at temperatures closer to $T_{g,liq}$, i.e. $T_D \geq 95$ K, essentially differs (see Figure 1d–h). Basically, this difference consists of two characteristics: (1) the absence of any exothermic effect at temperatures above T_D ; and (2) a large endothermic effect that peaks at a temperature $T_{g,dev}$ indicated with an arrow, higher than $T_{g,liq}$ as indicated with a dashed line. As T_D approaches $T_{g,liq}$, the temperature $T_{g,dev}$ at which the endothermic effect reveals its maximum first increases, exhibits the highest at $T_D = 105$ K, and then decreases toward $T_{g,liq}$ for the slowly cooled liquid.

Enthalpic Paths Followed by the Vapor-Deposited Glasses on Heating at ca. 40 mK min^{−1}. Figure 2a shows the enthalpic paths followed by the samples vapor-deposited at different temperatures T_D s and prepared by slowly cooling the liquid. The paths near the $T_{g,dev}$ s are shown on an enlarged scale in Figure 2b. The enthalpies were evaluated by summing directly the electrical energies intermittently supplied into the sample within the calorimeter cell under adiabatic conditions, against the temperatures increased consequently; the increment of the temperature after each energy supply is affected naturally by the enthalpy released or absorbed by the sample due to a relaxation phenomenon, as revealed in Figure 1, toward its equilibrium state. The thin lines in Figure 2a,b were so drawn as to link the data points smoothly by using a sigmoid function (ref 19). The enthalpies for the liquid-cooled glass, represented by black filled circles, could only be measured in the equilibrium supercooled state between 115 and 118 K without a

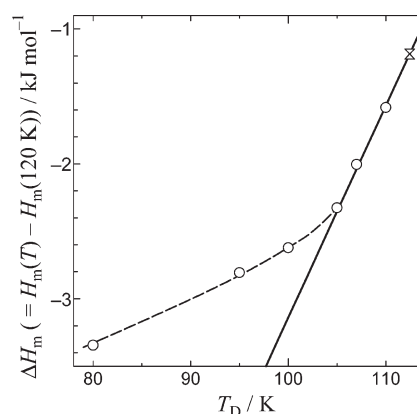


Figure 3. T_D dependence of the enthalpies of the glasses: straight line, dependence of the enthalpies for the equilibrium supercooled liquid; double triangles, liquid cooled glass; dashed line, a guide for the eyes to the enthalpies of the glasses vapor-deposited at temperatures below 105 K. The enthalpies above 105 K come close to the equilibrium values given at the respective T_D . Below 105 K, however, they deviate gradually from the equilibrium line.

spontaneous enthalpy-relaxation effect. Beyond 118 K, a small exothermic effect, attributed to crystallization initiation, started to be detected, and therefore, the exothermic effect was corrected in the evaluation of temperature increments in the range. The data in 115–118 K for the supercooled liquid were then fitted with a linear function in order to obtain the extrapolated low-temperature equilibrium linedrawn in Figure 2 with a thick dashed one. It was observed that despite the small exothermic spontaneous enthalpy drifts above 118 K, the enthalpy evaluated up to 121 K did not deviate from this linear fit extrapolated to higher temperatures; indeed, the exothermic effect only started to steeply increase around 123 K. In Figure 2, the enthalpies have been plotted as referred to the value at 120 K for the supercooled liquid. The enthalpies followed upon heating the as-deposited samples were set to match that of the supercooled liquid, above the respective temperatures where the spontaneous endothermic effects have disappeared as shown in Figure 1. The vapor-deposited glasses with $T_D \geq 95$ K were observed to display enthalpy curves, which were lower than that of the slowly liquid-cooled glass. The glass vapor-deposited at 105 K was found to be in the lowest enthalpic state among them. The temperature 105 K is close to the temperature at which the density maximum was observed,^{9,10} rather than 90–95 K observed by nanocalorimetry;¹¹ the reason is not clear at present. Only the sample with $T_D = 80$ K, represented by pink circles, was found to be in a higher enthalpic state than the liquid-cooled glass at low temperatures.

DISCUSSION

Enthalpic States of the Glasses at the Vapor-Deposited Temperatures, T_D s. The first calorimetric studies with an adiabatic calorimeter on vapor-deposited molecular glasses showed these entities to have high enthalpies on account of their highly disordered structure,^{15,17,18} as found for the glass vapor-deposited at 80 K in Figure 2a. The results for the other vapor-deposited glasses clearly demonstrate that this is not always the case as argued by some groups.^{1,2,9–12} Vapor-deposition of molecular glasses immediately below $T_{g,liq}$, i.e., in the range

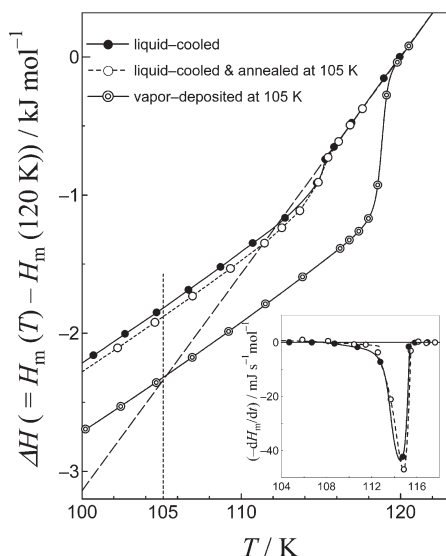


Figure 4. Comparison between the effects of long aging at 105 K and vapor-deposition at 105 K on the enthalpic stabilization of glasses: filled circles, sample cooled slowly at 10 mK min⁻¹; open circles, slowly cooled with additional aging at 105 K for 96 h on the cooling way; double circles, vapor-deposited at 105 K. Lines are guides for the eyes. The aging is found to yield little stabilization of the glass; namely, the origin of the low enthalpy of the vapor-deposited glass is in the deposition process itself.

$(0.79-0.96)T_g$, can produce glasses with enthalpic states lower than those for the liquid-cooled ones.

On the basis of the results of Figure 2a, Figure 3 shows the dependence of the enthalpies at the vapor-deposited temperatures T_D s; there, a double triangle mark represents the value for the slowly cooled liquid glass, and a solid line is the temperature dependence of the enthalpies extrapolated for the equilibrium supercooled liquid. Ishii and Nakayama among the present authors have recently argued for the formation of anomalously dense glasses, i.e., glasses with larger densities than those of the supercooled liquid, for ethylbenzene when $T_D \geq 0.87T_{g,liq}$.^{9,10} It is indicated from Figure 3 that the formation of corresponding anomalously low-enthalpic glasses was not observed in the present experiments. In fact, the enthalpy values at T_D s = 105, 107, and 110 K seem to be very close to the equilibrium, i.e., the linearly extrapolated supercooled-liquid values. This feature would apparently support the idea that these glasses could be understood as being equivalent to long-term annealed glasses rather than those bearing mixtures of novel metastable configurational states, as has been cogitated lately.⁴ If it is assumed that enthalpy should be linked to density in a one-to-one fashion, the question as to why the present enthalpy measurements have not detected the acclaimed anomalous dense amorphous states of ethylbenzene is at present unanswerable. In the view that enthalpy is expected to decrease with deposition rate ν_D , it is unlikely that this parameter was the cause of the discrepancy since ν_D for the present experiments was lower than that in the volume experiments.^{9,10} One of possible rationalizations may be connected with the differences in the deposition period or in heating speed for measurements. The present glass samples were prepared by continuing vapor-deposition for 96 h and amounted to about 0.5 mm thick. As a result, the samples were allowed potentially to relax toward their quasi-equilibrium states for a long enough time. However, the samples in volume measurements were prepared in a

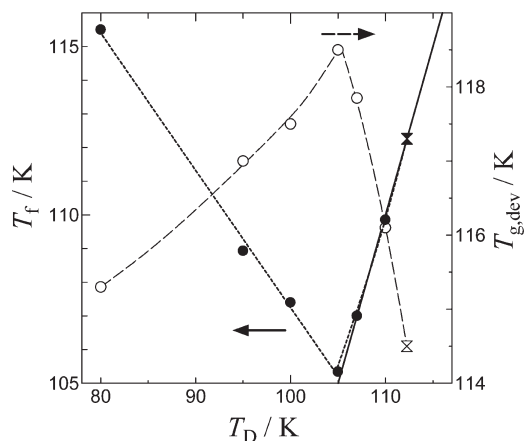


Figure 5. T_D dependence of the fictive temperatures T_f measured from the enthalpies and the most-sharply devitrifying temperatures $T_{g,dev}$ on heating the glasses: filled circles and double triangles, T_f ; open circles and double triangles, $T_{g,dev}$. A dotted and a dashed line are guides for the eyes to the T_f and $T_{g,dev}$ dependence, respectively. A solid line representing the relationship $T_D = T_f$ the T_f data above 105 K rather get on the line.

relatively short period and heated up at a relatively high speed of 0.28 K min⁻¹, whereas the speed was 40 mK min⁻¹ in the present measurements. It potentially resulted that the samples were rather in transient states and very far from their equilibrium states.

However, the values at $T_D < 105$ K deviate upward from the equilibrium line for the supercooled liquid; the deviation increases with decreasing the temperature. This behavior is consistent with the results of the first calorimetric studies with an adiabatic calorimeter on vapor-deposited molecular glasses.^{15,17,18} When vapor was deposited at much lower temperatures than $T_{g,liq}$, the glasses formed had higher enthalpies in view of their highly disordered structure. In this respect, the dashed line might increase at much lower T_D s than 80 K.

In order to gain some insight into the low-enthalpic nature of the glasses prepared via vapor-deposition near $T_{g,liq}$, it is instructive to compare the enthalpy values of the glass with $T_D = 105$ K against those of the two liquid-cooled glasses; the as-cooled one and the additionally aged one, which were subjected to an aging treatment at 105 K on the cooling way for the same amount of time as required by the vapor-deposition process, i.e., ca. 96 h. This comparison has been done in Figure 4 regarding the enthalpies and the temperature dependence of the rates of spontaneous enthalpy-relaxation. It may be observed that, on one hand, aging the liquid-cooled glass at 105 K for 96 h lowers the enthalpy of the liquid-cooled one only by ca. 0.07 kJ mol⁻¹; whereas, on the other hand, vapor-deposition at 105 K yields a glass that is ca. 0.51 kJ mol⁻¹ lower than the as-cooled liquid glass. Similarly, from the inset of Figure 4, comparison of the endothermic signals of the devitrification process for the as-cooled and additionally annealed liquid glasses consistently shows that aging does not considerably affect the endothermic peak: only a little sharpening and slight shift of peak maximum to higher temperature were observed. In the case of the vapor-deposited glass with $T_D = 105$ K, the endothermic peak greatly differed from that of the liquid-cooled glass (see Figure 1). These results, therefore, indicate that the low-enthalpic state of the vapor-deposited glass does not result from the structural aging, which inevitably occurs during the long depositing time.

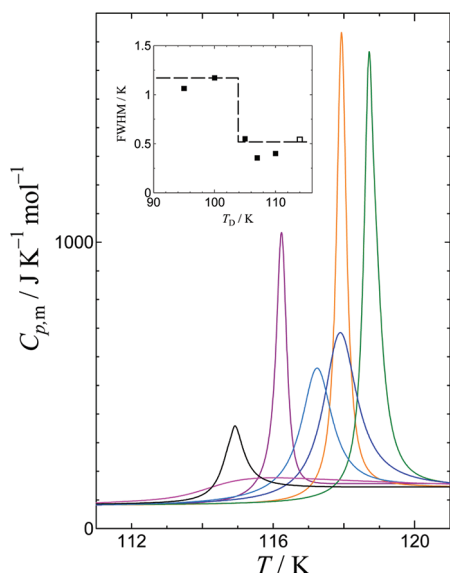


Figure 6. DSC-equivalent heat capacity curves, derived by differentiating the enthalpy paths in Figure 2 with respect to temperature, for the glasses vapor-deposited at different temperatures and the liquid-cooled glass: black line, liquid-cooled glass; pink line, $T_D = 80$ K; blue line, $T_D = 95$ K; deep blue line, $T_D = 100$ K; green line, $T_D = 105$ K; orange line, $T_D = 107$ K; purple line, $T_D = 110$ K glass. The heating rate is ca. 40 mK min^{-1} . The overshoot effect due to devitrification of the glasses strongly depends on the T_D . The inset shows the T_D dependence of the full width at half-maximum of the overshoot over the heat capacity curve of the supercooled liquid above the glass transition temperature. The dashed line is just a guide for the eyes.

Devitrification Behaviors Characteristic of the Glasses Vapor-Deposited near the $T_{g,liq}$. As stated above and seen from Figure 2, $T_{g,dev}$ s as a function of T_D show a maximum when $T_D = 105$ K. The values are plotted with open marks in Figure 5. Below $T_D = 105$ K, $T_{g,dev}$ slowly decreases until it approaches $T_{g,liq}$ as at $T_D = 80$ K. Above $T_D = 105$ K, however, it rather rapidly decreases to $T_{g,liq} = 114.5$ K. In Figure 5, the fictive temperature T_f estimated as the temperature at which the enthalpy curve for each vapor-deposited glass crosses the line for the supercooled liquid in Figure 2 is plotted with filled marks against the T_D as well. The value for the $T_D = 80$ K glass was estimated by using the dotted line drawn in reasonable parallel to the other lines in Figure 2. In Figure 5, a solid line represents that of $T_f = T_D$. T_f shows a minimum when $T_D = 105$ K and increases both below and above $T_D = 105$ K. The $T_{g,dev}$ and T_f thus display quite a contrast and have a strong correlation: the lower the T_f , the higher the $T_{g,dev}$. This means that the higher kinetic stability, i.e., higher $T_{g,dev}$ value, is connected to the more tightly packed glassy structure, i.e., lower-enthalpic state. This correlation agrees with the one just pointed out by other groups so far.^{1,2,9,10}

Here, it is noted that the change of the $T_{g,dev}$ and T_f with T_D is rather gradual when $T_D < 105$ K as compared with that when $T_D > 105$ K. In connection with this, as seen from Figure 2b, the devitrification rates taken as the ones at which the enthalpic state approaches the equilibrium line are steep when $T_D \geq 105$ K as compared to those when $T_D < 105$ K. The temperature dependence of the rates is alternatively represented by the heat capacity curves as should be observed by DSC at a very low heating-rate of 40 mK min^{-1} , as shown in Figure 6; the curves were evaluated by differentiating the enthalpic paths in Figure 2 with respect to temperature.

The accelerating devitrification effect is seen as the magnitude of the overshoots of the heat capacity curves. The shape of the overshoots looks different when $T_D < 105$ K and when $T_D \geq 105$ K. The inset of Figure 6 shows the full width at half-maximum (fwhm) of the overshoot over the heat capacity curve of the supercooled liquid above T_g . The fwhm clearly differs between the glasses with T_D s below and above 105 K; around 1.2 K when $T_D < 105$ and 0.6 K when $T_D \geq 105$ K. This clear difference might be related to the existence of some new glassy state pointed out by Dawson et al.⁸ The reasoning of the characteristic is critical for the understanding of the glasses prepared by vapor deposition immediately below the $T_{g,liq}$ and a subject to be clarified.

CONCLUSIONS

We have presented precise measurements of the enthalpic paths, fictive temperatures T_f and devitrification temperatures $T_{g,dev}$ for glassy ethylbenzene prepared by vapor-deposition at different temperatures T_D immediately below $T_{g,liq}$. The measurements, without doubt, confirm the low enthalpic nature of vapor-deposited molecular glasses when T_D is in the range $0.79\text{--}0.96T_g$ as compared to the enthalpic states of liquid-cooled glasses. The devitrification characteristic was indicated to differ between the glasses with $T_D < 105$ K and $T_D \geq 105$ K. It is intriguing that the character is clearly separated at $T_D = 105$ K where the glass with the lowest T_f was obtained.

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(19) Nonlinear regression was carried out using the sum of three functions: (1) a polynomial of second order, (2) an arctangent function allowing for asymmetry, and (3) an integrated logistic function. The two latter functions were chosen because their derivatives respectively give a peak and a step function and therefore may be used to characterize the C_p overshoots (see Figure 5) and the C_p jump during devitrification.