

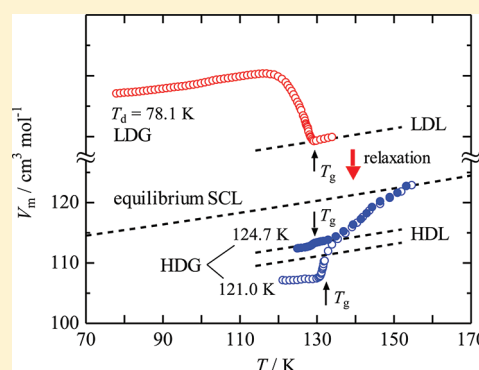
Nonequilibrium and Relaxation in Deeply Supercooled Liquid of Isopropylbenzene Obtained through Glass Transition from Vapor-Deposited Glass

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Supporting Information

ABSTRACT: Change in the light interference in film samples of isopropylbenzene was studied in the supercooled liquid (SCL) state. Samples were originally formed as glass by vapor deposition on a cold substrate and the intensity of laser light reflection from them was monitored as the temperature was raised with a constant rate up to the region of the SCL state above the glass-transition temperature. Two types of periodic changes in the light intensity were observed in the SCL state. One was attributed to the interference condition change accompanying the structural relaxation from the low-density SCL to the equilibrium SCL state, and the other was due to the gradual expansion of the high-density SCL. Analysis of the latter change revealed that the initial density of the high-density glass was larger than that estimated in our previous paper.



1. INTRODUCTION

It has been implicitly considered that a single-component liquid has only one liquid phase. However, since the liquid–liquid (L–L) transition in phosphorus was identified at high pressure and high temperature,^{1–3} it has been accepted that even a single-component liquid can have multiple liquid phases. L–L structural transformations have also been reported for molecular systems such as triphenyl phosphite (TPP)^{4,5} and butyl alcohol⁶ in supercooled liquid (SCL) states, although these phenomena still seem to be open to further discussion. In addition, the possible existence of two SCL phases of water has been suggested^{7,8} on the basis of the experimental evidence of an amorphous–amorphous transition.^{9,10} Liquid polymorphism has thus attracted attention as a new field of study on liquids, and we recently proposed the term polyliquidism to describe such phenomena.¹¹

Ediger and co-workers^{12–16} have extensively studied various properties of vapor deposited molecular glasses using indomethacin (IMC) and tris-naphthylbenzene (TNB) as target compounds. They found that highly stable glasses were obtained by vapor deposition with the deposition temperatures (T_d) close to glass transition temperature (T_g). Rodriguez and co-workers^{17,18} conducted in situ thermal studies on vapor-deposited TL and EB using a nanocalorimetric system and obtained similar results on the enthalpy change of glasses to those reported by Ediger and co-workers.

We have studied the properties of vapor-deposited glass of toluene (TL), ethylbenzene (EB), propylbenzene (PB), and isopropylbenzene (IPB) using laser-light interference in film samples.^{19–22} The density and relaxation behavior of these glasses proved to be systematically dependent on T_d .^{21,22} The initial glass samples of each compound deposited at T_d much

lower than T_g had lower densities than that expected for the SCL at the same temperature. In contrast, glass samples deposited in a narrow temperature region close to T_g had higher densities than that expected for the SCL at the same temperature, which is in harmony with the findings by Ediger and co-workers on the stable glasses of IMC and TNB. Thus, the T_d -dependence of the properties of vapor-deposited molecular systems is a general issue, although actual features may be dependent on the molecular structure of each compound. We referred to two types of our vapor-deposited glasses as low-density glass (LDG) and high-density glass (HDG), respectively.²²

Considering our previous studies on the behavior of vapor-deposited glasses of benzene derivatives,^{11,21,22} LDG and HDG exhibited a difference in relaxation behavior when their temperatures were raised with a constant rate. LDG displayed shrinkage before the glass transition, while HDG underwent expansion before the glass transition. Thus, LDG is considered to incorporate a highly disordered structure with a large excess volume, while HDG is considered to incorporate some compact intermolecular packing in the disordered structure. In addition to these points, the most remarkable finding on the vapor-deposited samples of EB, PB, and IPB was that the structural difference due to the difference in T_d was maintained even in the SCL state above T_g .^{11,22} This was determined from the change in the intensity of laser-light reflected from film samples. SCL appearing from LDG of EB, PB, and IPB exhibited a significant

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depression in the intensity of reflected light, while SCL appearing from HDG of these compounds did not. We thus considered that LDG and HDG turned into SCLs with different structures above their T_g , i.e., samples originally formed as LDG may keep a memory of the LDG structure in the SCL state to some extent, and samples originally formed as HDG may similarly keep a memory of the HDG structure in the SCL state. We refer to the former-type SCL as the low-density liquid (LDL) and the latter-type SCL as the high-density liquid (HDL).²²

We confirmed that the depression in the reflected-light intensity exhibited by LDL was caused by light scattering.^{22,23} In addition, the appearance of the depression was irreversible²⁴ and was accompanied with a small enthalpy decrease that was almost proportional to the sample thickness.¹¹ Thus, we have previously considered that LDL was less stable than HDL in the temperature region close to T_g and that LDL relaxed to HDL when the temperature was raised to some specific point.²² The light scattering that accompanies the relaxation behavior of EB, PB, and IPB in the SCL state was thus considered to be due to the bulk inhomogeneity of the refractive-index caused by the temporal coexistence of LDL and HDL. Although the sample preparation method was different from the vapor deposition, similar light scattering due to long-range density fluctuation in SCL states was observed for orthoterphenyl, and the appearance of such fluctuation was dependent on the thermal history of the sample.²⁵

In this article, we report the results of further examination of the intensity change of light reflected from IPB samples in the SCL state. IPB samples exhibit two types of periodic change of the reflected-light intensity in the SCL state, which are dependent on the presence/absence of the significant depression of light-intensity. Analysis of these observations leads to a revision of the vertical scale of the diagram that represents the volume change accompanying the relaxation of IPB samples.²²

2. EXPERIMENTS AND DATA ANALYSIS

The apparatus and experimental methods were essentially the same as those previously described.^{20,22} Regent grade IPB (Tokyo Chemical Industry) was used after purification by distillation and fractional crystallization. Glass samples approximately 10 μm thick were prepared by vapor deposition on a gold-plated copper substrate mounted on a coldfinger. The base pressure in the vacuum chamber was approximately 10^{-7} Pa. Samples were deposited at a rate of ca. 0.2 $\mu\text{m min}^{-1}$. After deposition, the sample temperature was raised at a constant rate of 0.28 K min^{-1} . The intensity of laser light (514.5 nm light of an Ar^+ laser) reflected from the sample was measured using a silicon photocell to estimate the sample thickness during vapor deposition and to monitor the structural evolution of the sample during temperature elevation. These measurements were based on the assumption of light interference as described in the next paragraph. Raman spectra of the sample were also measured simultaneously with the reflected light intensity to monitor the sample state, although the spectra are not discussed here. The incident angle of the laser light was 60° from the normal to the substrate, and the laser power was 30 mW at the outside of the inlet port of the vacuum chamber.

Analysis of the light interference in the film sample was performed using the previously described method.^{20,22} The concept of light interference is schematically shown in Figure 1. During vapor deposition, we counted the number (N) of so-called interference fringes and estimated the sample thickness

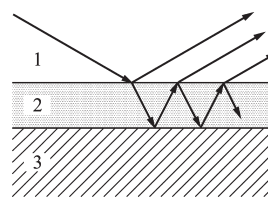


Figure 1. Schematic diagram of the reflection and interference of laser light at a vapor-deposited film on a metal substrate. 1, vacuum; 2, sample film; 3, metal substrate.

(d) using eq 1 assuming a constant and isotropic refractive index (n) for the sample.

$$N = \frac{2d}{\lambda} \sqrt{n^2 - \sin^2 \theta} \quad (1)$$

where λ is the wavelength of laser light in a vacuum, and the refractive index of the vacuum is assumed to be unity.

As the sample temperature is increased after the vapor deposition, d and n generally change due to the structural change of the sample. Therefore, it was assumed that the interference fringe continued virtually into the region beyond the point where the vapor deposition was stopped and assumed that a point, which represented the sample state, moved forward or backward on the interference fringe accompanying the structural change. Thus, in the analysis, the change in the molar volume (V_m) of the sample was calculated from the observed movement of the state point on the fringe. For this, we first assumed a uniaxial change of the sample volume in the direction of thickness. We considered that this assumption was justified for a thin (about 10 μm thick) film of a soft material on a metal substrate with the lateral size of the order of ten millimeters. Second, the Lorentz–Lorenz equation (eq 2) was assumed, which includes n and V_m of the sample, and the so-called molecular refraction (R_M) was also assumed to be a constant for IPB. R_M of a small aromatic compound is not considered to be significantly influenced by the difference in the sample state, so far as disordered states such as glasses or liquids are concerned.²⁶ Similarly, n of vapor-deposited samples may be assumed to be isotropic in such disordered systems of small aromatic compounds, although structural anisotropy is sometimes observed for the vapor-deposited samples of compounds with large and anisotropic molecular structures.^{15,27}

$$R_M = \frac{n^2 - 1}{n^2 + 2} V_m \quad (2)$$

To estimate R_M for IPB, literature data for the density²⁸ and refractive index²⁹ of the room temperature liquid were employed. Note that the reliability of the results of V_m obtained by our analysis is primarily limited by the above assumptions.

3. RESULTS AND DISCUSSION

3.1. Interference Fringe of Reflected Light. Figure 2 shows the evolution of the reflected light intensity observed for IPB samples during the temperature elevation after vapor deposition at various T_d . Figure 2a,e displays the same data used in our previous paper,²² while the other panels display the newly obtained data. The symbols G, L, and C represent the glass, SCL, and crystalline states, respectively. These assignments are essentially based on consideration of the phase shift of the state

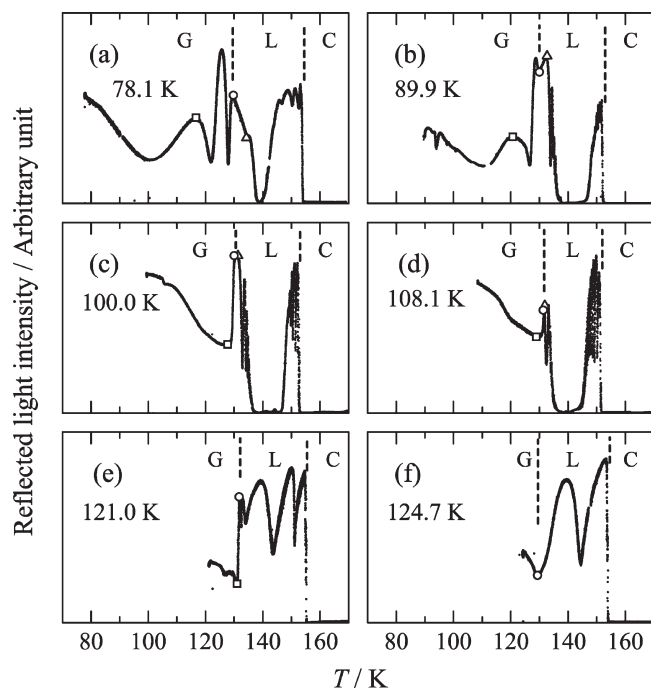


Figure 2. Evolution of light intensity reflected from film samples deposited at different temperatures as indicated in each panel. G, L, and C indicate the temperature region of the glass, SCL, and crystal states, respectively, experienced by each sample as the temperature was increased with a constant rate of 0.28 K min^{-1} . Open squares, the temperature at which the glass sample changed from gradual thermal expansion to a structural change due to relaxation in the glass state; open circles, T_g ; open triangles, the temperature at which SCL changed from thermal expansion to shrinkage, which is related to the relaxation in the SCL state.

point on the interference fringe observed during vapor deposition at constant temperature (see Figure 3a, for example) or during the temperature elevation after deposition (see, for example, the first half of the intensity evolution shown in Figure 2a). The details of these assignments have been described in our previous papers,^{11,20–22} and also in the Supporting Information for this article. Considering the interference fringes shown in Figure 2, the samples studied can be classified into three groups: the sample initially prepared as LDG at a sufficiently low T_d (Figure 2a), the samples initially prepared as LDG at intermediate T_d (Figure 2b,c,d), and the samples initially prepared as HDG at T_d close to T_g (Figure 2e, f). The characteristics of the fringe of each class are described later.

The open squares in Figure 2 represent the characteristic temperatures (T_r) at which the gradual increase of V_m due to thermal expansion of the glass becomes a rapid change (decrease or increase) due to structural relaxation.^{21,22} The sample deposited at 78.1 K (Figure 2a) is considered to have originally been in the LDG state and exhibited a rapid decrease of V_m during the relaxation process.²² In contrast, the samples deposited at 121.0 and 124.7 K (Figures 2e and f, respectively) are considered to have originally been in the HDG state, and exhibit rapid increases of V_m during the relaxation process.²² It should be noted that the samples deposited at 89.9, 100.0, and 108.1 K, the temperatures in the intermediate region, exhibit relaxation behavior in the glass state essentially similar to that of LDG (Figures 2b, c, and d, respectively), but these samples also exhibit interesting changes

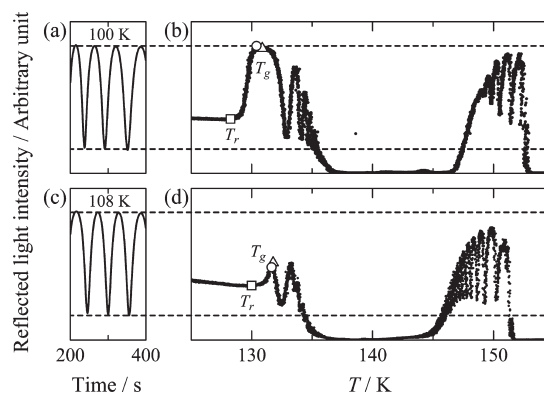


Figure 3. Comparison of the curve shape for reflected-light intensity recorded during vapor deposition and temperature elevation; samples deposited at 100.0 K (a, b) and 108.1 K (c, d). Dashed lines are guides for comparison of the light intensity data in panel b with that in panel a and the data in panel d with that in panel c. The open squares, circles, and triangles represent the same as those indicated in Figure 2.

of the reflected light intensity in the SCL state, as discussed in the next section.

The open circles in Figure 2 represent T_g for each sample. Although T_g is slightly dependent on T_d , it is located in a narrow region from 129 to 132 K. The observed changes of the reflected light intensity are attributed to changes in the interference condition of the laser light, except the significant depression around 140 K and the abrupt decrease in the region from 151 to 155 K. The significant depression will be discussed in the next paragraph. Regarding the abrupt decrease, X-ray and Raman measurements have indicated that this is due to crystallization of the sample.²⁴ Therefore, the samples are considered to have been in SCL states in the temperature region between T_g and the crystallization temperature. Since the sample vapor was not supplied during the temperature elevation, and since the vapor pressure of IPB in the temperature region displayed in Figure 2 is sufficiently small as discussed later, the complicated changes in the reflected light intensity observed for the SCL states, except the depression around 140 K, were due to correlative changes in the thickness and refractive index of the sample. In the present article, we concentrate our attention on such changes in the SCL states.

The significant depression of intensity around 140 K was observed for samples deposited at lower or intermediate T_d , as shown in Figure 2a–d. Similar intensity depressions were observed for EB and PB samples deposited at temperatures much lower than T_g of each compound. We have confirmed that this intensity depression is due to light scattering²³ and proposed that it accompanied the relaxation process from a SCL state to another SCL state.^{11,22}

Another remarkable phenomenon to which we direct our attention in this article is the short-interval periodic intensity changes before and after the significant intensity depression, as shown in Figure 2b–d, which show the results for IPB samples deposited at T_d in the intermediate region. Similar periodic intensity changes before and after the significant depression were occasionally observed for EB and PB samples,²⁴ although the phenomenon was not as clear as that for IPB.

In addition to the above features shown in Figure 2b–d, different types of periodic intensity changes of the reflected light were observed, as shown in Figure 2a,e,f. The sample deposited at

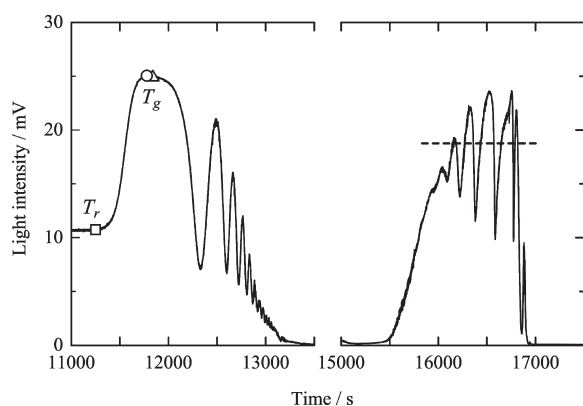


Figure 4. Detail of the evolution of reflected-light intensity recorded during temperature elevation of the sample deposited at 100.0 K. The light intensity data are the same as that shown in Figure 3b. Note that the abscissa in this figure represents the time, while that in Figure 3b represents the temperature. The horizontal dashed line indicates the average level of light intensity observed during vapor deposition of the sample.

78.1 K (Figure 2a) had a small-amplitude periodic intensity change following the depression around 140 K. The temperature interval of this periodicity was larger than those presented in Figure 2b–d. Thus, the change seems to be related to a structural change rather than that related to the short-interval periodic changes presented in the latter panels. It should also be mentioned that the samples deposited at 121 and 124.7 K (Figure 2e,f), of which T_d was close to T_g , exhibited periodic changes of much wider temperature intervals without significant intensity depressions.

3.2. Features of Interference Fringes Observed in SCL States of Samples Deposited at 100.0 and 108.1 K. Figure 3 shows the detailed interference fringes recorded during the initial period of vapor deposition at 100.0 and 108.1 K (Figure 3a and c, respectively) along with the reflected light intensity recorded for the corresponding samples during temperature elevation in the SCL state (Figure 3b and d, respectively). The shapes of the fringes recorded during vapor deposition are not sinusoidal but have characteristically round tops and sharp bottoms. This is understandable if we assume multiple reflections of the laser light in the film samples,³⁰ as described later using eq 3. These initial fringe data were used as a reference in considering the features of the interference patterns because each sample in the initial period is considered to have had good interference conditions in the film transparency and the surface smoothness. Although the ordinate of the panels in Figure 3 represents the output voltage of the light-intensity monitor in arbitrary units, the left and right panels for the same sample were plotted on the same scale. We thus constructed dashed lines that indicate the top and bottom positions of the fringes in Figure 3a,c and extended them into Figure 3b,d in which the changes of light intensity due to the temperature elevation are presented.

Before going into the detail of the interference fringe in the SCL state, we must consider the possibility of sample evaporation as a possible cause of the change in the interference condition because these experiments were conducted in a vacuum. Clear evidence was obtained in the recorded fringes that the evaporation of IPB samples was more pronounced above 180 K after melting of the crystal.²⁴ Moreover, the temperature interval of the periodic changes around 150 K (Figure 3b,d)

increased with temperature, which is contrary to the expectation based on the increase of vapor pressure with temperature. Therefore, we consider that the periodic changes observed in the SCL states are attributable to some other changes in the sample state.

Now, we concentrate our attention on the periodic changes of the reflected light intensity observed in advance of the depression around 140 K. The data displayed in Figure 3b,d indicate that these periodic changes begin almost immediately after the glass transition at the point indicated with an open circle. Unfortunately, the data in Figure 3b,d include the fluctuations in the temperature measurement along with the fluctuations in the light intensity measurement, and thus the periodicities of the light intensity changes are not clear. Therefore, the light intensity data of Figure 3b was plotted in a time series, as displayed in Figure 4. Figure 4 clearly shows that the periodic change occurred more than ten times in advance of the significant depression, which accelerated the change, decreased the amplitude, and diminished the average intensity toward zero with temperature. However, the periodic change following the depression around 140 K appeared after the light intensity recovered to the average level of the fringe observed during the initial vapor deposition (dashed line on the right-hand side of Figure 4). The latter periodic change then occurred approximately five times in advance of the other change related to the crystallization of SCL. In contrast to the change that occurred before the depression, the periodicity after the depression was slowed down with temperature, increasing the amplitude and keeping an approximately constant average intensity. Similar results were obtained by plotting the light intensity data of Figure 3d in a time series.

If the sample film was transparent and homogeneous in thickness, the interference fringe caused by the changes in the refractive index and/or thickness would show mainly a phase shift without a variation of the amplitude. Therefore, the changes in light intensity shown in Figure 4 before and after the significant depression imply that there was light scattering due to the appearance of bulk inhomogeneity of refractive index and also the appearance of surface roughness accompanying the structural relaxation. These points are discussed in the next two sections.

3.3. Qualitative Consideration of the Interference Fringe Shape. To illustrate the feature of the interference fringe shape, we consider eq 3, which expresses the total amplitude (E) of the electric field of light multiply reflected from a dielectric film formed on a flat metallic substrate.³⁰

$$E = E_0 \frac{r_{12} + r_{23}\xi e^{-i\delta}}{1 + r_{12}r_{23}\xi e^{-i\delta}} \quad (3)$$

The geometrical concept of this model is depicted in Figure 1. Here, E_0 is the initial amplitude of the incident light field, and the subscripts 1, 2, and 3 indicate the vacuum space, dielectric film, and metal substrate, respectively. r_{ij} is the reflection coefficient at the interface between the media indicated by the subscripts and is the function of the refractive indices of the corresponding media and the angle of the incident light. δ and ξ are the phase shift and attenuation coefficient of the light field during a downward-and-upward unit travel of the light across the film, respectively. δ is proportional to the optical thickness of the film. The observed intensity of the reflected light is proportional to EE^* .

We calculated EE^* for films with different optical properties as a function of δ . Figure 5 shows typical shapes of the interference curve obtained from such calculations. In these calculations, we

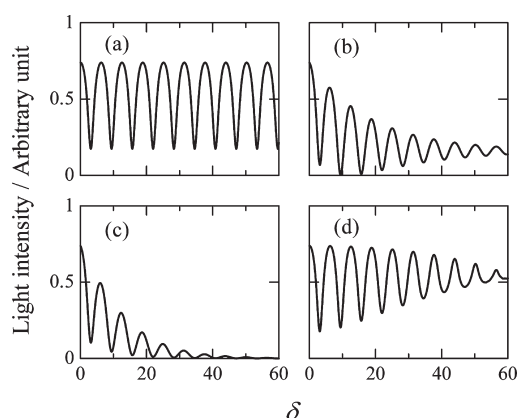


Figure 5. Model shapes of the interference fringe calculated using eq 3 under the different interference conditions described in the text. The common quantity δ of the abscissa in each panel corresponds to the phase difference between the reflected light waves with optical path lengths different by one unit of travel in the film sample (see Figure 1).

assumed that $E_0 = 1$, $r_{12} = -0.4$, and $r_{23} = -0.7$ to qualitatively reproduce the shape of the interference fringes observed for IPB samples. The curve in Figure 5a was calculated assuming ξ in eq 3 to be unity, which corresponds to the case of a film with perfect transparency. The calculated periodic curve is characterized by round tops and sharp bottoms and reproduces well the data recorded in the initial period of vapor deposition of the IPB samples (Figures 3a,c).

Next, the effect of ξ was examined by assuming it to be $e^{-0.05\delta}$, and the resulting curve is shown in Figure 5b. IPB does not absorb light with the wavelength used in our measurements (514.5 nm). Therefore, the second example corresponds to the case where the incident light is scattered during travel within the film. It should be noted that the curve in Figure 5b converges to the value of r_{12}^2 and that the reflected light is not diminished completely, so far as the reflectivity at the sample surface is kept constant.

EE^* was then examined by assuming r_{12} to be $-0.4 e^{-0.05\delta}$ and ξ to be $e^{-0.05\delta}$. The resulting curve is presented in Figure 5c. This corresponds to the case where the scattering of incident light at the film surface increases with the sample thickness along with the bulk scattering. In this case, the curve converges to zero in contrast to Figure 5b. Such cases were encountered during the vapor deposition of chlorobenzene.³⁰

Finally, the effect of spatial inhomogeneity of δ , which represents the optical thickness, was examined. For this purpose, the right-hand side of eq 3 was rewritten with an average of five terms each with the same form as in eq 3, with the value of ξ equal to unity, but the parameter representing the phase shift assumed to be one of the five values from $0.96i\delta$ to $1.04i\delta$. The result is shown as the curve in Figure 5d. The characteristic feature of this curve is that it converges to the value that is the average of the interference fringe expected for the case of homogeneous thickness.

3.4. Interpretation of Observed Evolution of Reflected Light Intensity. We now reconsider the evolution of reflected light intensity experimentally observed for IPB samples (Supporting Information). In this section, we discuss the behavior of IPB samples by classifying the data into three groups as mentioned in section 3.1.

The first case is the evolution observed for the sample originally vapor-deposited as LDG at a sufficiently low T_d

(78.1 K, Figure 2a). T_g for this sample was apart from T_r , and the reflected light intensity had the characteristic feature of an interference fringe for approximately one and a half cycles between these temperatures. During this temperature elevation process, the state point on the interference fringe is considered to have exhibited a backward motion on the fringe, and the sample in the glass state is considered to have undergone structural relaxation with accompanying shrinkage. In the next temperature region immediately above T_g , the sample in the SCL state is considered to have exhibited a forward motion of the state point on the fringe accompanied with thermal expansion. At 135 K (open triangle), the thermal expansion changed to shrinkage. Immediately after this change, the relaxation from LDL to another SCL took place as indicated by the significant depression of the reflected light intensity.^{11,22} Note that this depression is not due to the change in the interference condition but is due to light scattering mainly in the bulk of the sample.¹¹ In addition, it should be emphasized that no indication of crystallization could be detected in this temperature region from Raman spectra and X-ray diffraction patterns.²⁴ When relaxation to the new SCL was almost completed, the transparency of the sample was recovered to half the level of the maximum intensity. Following this, a periodic change with small amplitude began at approximately 146 K, which repeated for approximately three cycles increasing slightly its amplitude. The feature of this periodicity is the inverse of the curve in Figure 5d, which suggests that the inhomogeneity in the optical thickness of the sample was gradually dissipated. The sample then began crystallization at 154 K.²⁴

The second case is the behavior observed for the samples that were vapor-deposited at 89.9, 100.0, and 108.1 K; the T_{ds} in the intermediate region. The separation between T_r (open squares) and T_g (open circles) of these samples was small, as shown in Figure 2b–d, Figure 3b,d, and also in Figure 4. Similarly, the separation between T_g and the turning point in the SCL state from thermal expansion to shrinkage is considered to have been small. We estimated the positions of these points at the temperatures indicated with the open triangles shown in these figures. Note that the temperatures of the three different symbols are close to each other, and their correct positions could not be precisely indicated in Figure 2c,d. The periodic changes that occurred in the SCL state in advance of the significant depression around 140 K are considered to be due to rapid shrinkage of the samples accompanied with an increase of the refractive index and are considered to be the phenomena that leads LDL to another SCL.^{11,22} The feature of the above periodic changes is more clearly shown in the left-hand side of Figure 4, as mentioned in section 3.2, and is similar to that shown in Figure 5c. Therefore, the L–L relaxation was a process in which both the bulk and surface scattering increased along with the decrease in the optical thickness.

We cannot assume light interference in the sample in the temperature region of the depression since it was caused by light scattering. When the L–L relaxation came to the final stage, the transparency of the sample was recovered to a level of approximately half that of the as-deposited sample, and the sample again began to exhibit interference of the light. Thus, another periodic change of light intensity was observed for many cycles with increase of its amplitude (see the last parts of Figure 3b,d and Figure 4). The feature of these changes, that is the recovering amplitude of the periodic change, was the inverse of the curve in Figure 5d. This indicates that the inhomogeneity in the optical thickness of these samples was gradually diminished as the

temperature was increased. After such changes, crystallization of the samples began in the temperature region from 152 to 154 K. Note that the amplitude of the periodic change just before the start of crystallization was larger for the sample originally prepared at higher T_d , which suggests that the effect of sample thickness inhomogeneity formed during vapor deposition of the glass sample remains even in the SCL state after experiencing several relaxation processes.

The third case of evolution of the reflected light intensity in the SCL state was the behavior observed for the samples deposited at 121.0 and 124.7 K (Figure 2e,f). These samples were originally prepared as HDG during vapor deposition and exhibited volume expansion when the structural relaxation occurred in advance of the glass transition. After the glass transition, they had a few cycles of the interference fringe with a very large temperature interval until crystallization occurred at approximately 155 K. Note that these samples exhibited no significant depression of the reflected light intensity around 140 K. Thus, the entire evolution of the reflected light intensity in the SCL state may be attributed to continuous changes in the interference conditions. The record of reflected light intensity observed for the sample deposited at 124.7 K (Figure 2f) has a feature expected for an interference fringe such as the curve in Figure 5a. Therefore, we consider that this sample exhibited continuous expansion in the entire region of the SCL state. If we apply our model of light interference to the approximately 1.5 cycles of the fringe shown by this sample, then the relative thermal expansion $\Delta V/V(T_g)$ between T_g and the temperature of crystallization is 0.084. This value is apparently larger than the value of 0.021, which is expected for the thermal expansion inferred for the equilibrium SCL state of IPB in the corresponding temperature interval. Therefore, we consider that the SCL state of this sample just after the glass transition has a small volume in a nonequilibrium state and that the sample exhibits a larger expansion during the temperature elevation than that expected for SCL in the equilibrium state. If we could assume that the SCL state of this sample just before the start of crystallization was the equilibrium SCL state of IPB, then the V_m of the SCL state of this sample just after the glass transition would be smaller by 7.9% (higher density) than that expected for SCL in the equilibrium state at the same temperature.

The sample deposited at 121.0 K (Figure 2e) had an evolution of the reflected light intensity similar to that shown for the sample deposited at 124.7 K. However, this sample also exhibited anomalously rapid decreases of light intensity at approximately 132.5 and 151 K. The cause of these decreases is not clear at present, but some accidental strain might cause an optical inhomogeneity of the sample and bring about a decrease of the light intensity. If we could neglect these accidental decreases, this sample exhibited approximately 2.2 cycles of the interference fringe in the temperature interval from T_g to the crystallization temperature. Thus, V_m of this sample just after the glass transition may have been slightly smaller (higher density) than the corresponding value of the sample deposited at 124.7 K under the same conditions.

3.5. Importance of the Present Findings on Vapor-Deposited Molecular Glasses and Supercooled Liquids. We have previously reported that the behavior of SCL samples of EB, PB, and IPB obtained through the glass transition of vapor-deposited glasses is dependent on the deposition temperature of the original glass.^{11,21,22} As a consequence of these studies, we previously inferred that LDL obtained from LDG was in a

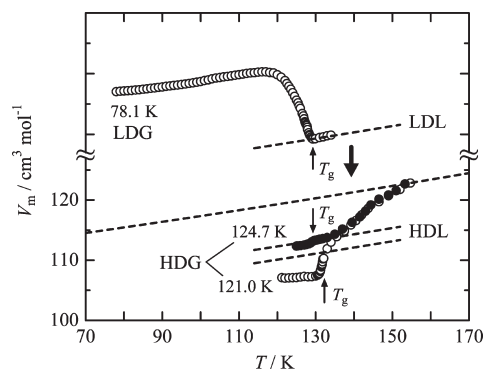


Figure 6. Mutual relationship of the temperature dependence of V_m for IPB samples vapor-deposited at different temperatures. We propose this diagram as a revision of the corresponding diagram for IPB previously given in ref 22. Closed circles indicate the evolution of V_m for the sample initially deposited as HDG at 124.7 K. Open circles in the lower part of the figure indicate the evolution of V_m for the sample initially deposited as HDG at 121.0 K. Open circles in the upper part of the figure indicate the evolution of V_m for the sample initially deposited as LDG at 78.1 K. Note that we can indicate values for the lower part of the ordinate on the basis of the light interference analysis; however, the values for the upper part of the ordinate have been left blank, due to the lack of continuity of the interference data. Small arrows indicate T_g for each sample. The large arrow indicates the temperature region and direction of the V_m change at the L–L relaxation exhibited by the sample initially deposited as LDG. The longest dashed line indicates the extrapolation of the temperature dependence of V_m for IPB liquid (ref 28). Other short dashed lines represent the levels of V_m for each sample after the glass transition (LDL or HDL) and are guides to qualitatively indicate the thermal expansion of each SCL.

nonequilibrium SCL state and relaxed into another SCL, which was HDL directly obtained from HDG. We thus came across an issue that more than one curve of the temperature dependence of V_m for the SCL state had to be assumed.²²

In addition to this issue, the results of the present studies have revealed that HDL obtained through the glass transition of vapor-deposited HDG is in a nonequilibrium state in the early stage after the glass transition and that HDL undergoes gradual relaxation with continuous expansion by temperature elevation. Therefore, the multiple SCL states of vapor-deposited molecular samples are complex phenomena that involve a variety of nonequilibrium SCL states.

We described in the last part of the previous section that V_m of HDL after the glass transition from HDG was smaller than that expected for the equilibrium SCL at the same temperature. Taking these results into account, we present a schematic diagram in Figure 6 that represents the mutual relationships among the evolutions of V_m for the vapor deposited IPB samples. The longest dashed line represents the extension of the temperature dependence of V_m for the equilibrium IPB liquid.²⁸ The evolution of V_m for the sample deposited at 124.7 K is plotted with closed circles in Figure 6 from analysis of the interference fringe shown in Figure 2f. Here, we assumed that V_m at the start of crystallization coincided with the extension of the data for the equilibrium liquid and traced the interference fringe backward lowering the temperature. The short dashed line attached to the plot with the closed circles represents the level of V_m that was assumed by the sample after the glass transition, and indicates the trend for the thermal expansion of the HDL.

Similarly, the open circles in the bottom part of Figure 6 plot the V_m data for the sample deposited at 121.0 K. We analyzed the interference fringe (Figure 2e) by neglecting the anomalies at approximately 132.5 and 151 K. The level of V_m obtained for this sample just after the glass transition is located lower than that for the sample deposited at 124.7 K, which also suggests that the initial V_m in the glass state of this sample at the vapor deposition is smaller than the value we previously considered without taking account of the large expansion in the SCL state.²² Unfortunately, V_m of IPB in the crystal state has not yet been determined. However, the V_m data of TL in the liquid and crystalline states^{28,31,32} suggest that V_m of the densest HDG of IPB could be comparable to that of its crystal state.

In contrast to the cases of samples initially formed as HDG, we cannot logically estimate V_m for the samples that were initially formed as LDG and changed into LDL after the glass transition. This is because the continuity of the interference fringe of such samples is broken at the temperature of the significant depression around 140 K. The data for the sample deposited at 78.1 K is temporally plotted with open circles in the top part of Figure 6. However, to continue the plot beyond the region of 140 K and compare the V_m at the start of crystallization with that of other samples requires that we determine the volume change accompanying the L–L relaxation, which is represented by a large downward arrow in Figure 6. We have thus left the values for the vertical scale blank in the upper part of Figure 6, although the interval of the scale is the same as for the lower part of this figure.

The formation of anomalously stable molecular glasses by vapor deposition at temperatures close to T_g has attracted much attention.^{12–18,33–35} Our findings of HDG vapor-deposited at T_d close to T_g are in harmony with the formation of low-enthalpy glasses observed by Ediger's group,^{12–16} in spite of the large difference between the molecular sizes of the compounds used in our and their studies. The results by Rodriguez and co-workers^{17,18} on the enthalpy changes of TL and EB samples seem essentially the same as those of Ediger's group, but it should be noted that their T_g shifted to a much higher region than that observed previously.^{22,36} It may be due to the very fast temperature elevation in their experiments. Singh and de Pablo³⁵ studied the density of vapor-deposited glasses of trehalose by the method of molecular simulation and found the formation of low-enthalpy samples at a particular region of T_d and also found a correlation of thermal stability with density. Thus, our new results shown in Figure 6 on IPB samples may provide a clue to discuss the relationship between thermal stability and structure of vapor-deposited molecular glasses.

Finally, we should mention our present view regarding the behavior of the samples deposited at 89.9, 100.0, and 108.1 K. These samples, which were deposited at intermediate T_d , exhibit complex behavior, as shown in Figures 2, 3, and 4. All of these samples exhibit the significant depression of reflected light around 140 K. Therefore, they are considered to have taken the LDL state immediately after the glass transition. However, the appearance of this depression has prevented the continuous analysis of the interference fringe in the entire range of the SCL state. Thus, a substantial estimation of V_m for these samples is presently impossible. In addition, it should be noted that the number of repetitions of the interference fringe before and after the significant depression is fairly large. If we applied our simple method of analysis, these numbers of repetition would suggest that an unreasonably large change in V_m accompanied the L–L

relaxation. Therefore, this issue requires further careful examination of the interference fringes.

4. CONCLUSIONS

We have reported that careful inspection of the evolution of laser light intensity reflected from vapor-deposited molecular samples sometimes enables the estimation of V_m , not only in the glass state but also in the SCL state. Samples were originally formed as glass by vapor deposition on a cold substrate, and the intensity of reflected laser light was monitored as their temperatures were increased with a constant rate up to the region of the SCL state above T_g . Two types of periodic change of the light intensity were observed for IPB samples in the SCL state. One was attributed to an interference-condition change accompanying structural relaxation from LDL to another SCL, and the other was due to the gradual expansion of HDL. These observations indicate that nonequilibrium states can be maintained at least for a few hours in deeply supercooled liquids obtained through glass transition from vapor-deposited glasses. Analysis of the gradual expansion of HDL enabled estimation of the volume increase between T_g and the temperature of crystallization for the samples initially formed as HDG during vapor deposition. These results revealed that the initial density of HDG was larger than that estimated in our previous papers.

■ ASSOCIATED CONTENT

S Supporting Information. Method of assignments of specific points on interference fringe. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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