

Excess Volume of Vapor-Deposited Molecular Glass and Its Change Due to Structural Relaxation: Studies of Light Interference in Film Samples

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A novel method for estimating the refractive index and density of vacuum-deposited molecular glasses was invented. It is based on the analysis of the interference of the light transmitted through film samples. Molar volumes of toluene, ethylbenzene, and propylbenzene in the glass states were thus elucidated. The volume just after the sample deposition at 78 K was larger by 4–10%, depending on the size of the substituent on the phenyl ring of each compound, than the fictitious value for the supercooled liquid estimated at the same temperature. By temperature elevation at a constant rate, the volume increases first by the thermal expansion of the glass and next decreases rapidly in a narrow temperature region just below the glass-transition temperature. This decrease is attributed to the structural relaxation in the glass, and its magnitude is related to the size of the substituent. Excess volumes included at the initial sample deposition are discussed in relation to the excess enthalpies reported for similarly prepared molecular glasses.

1. Introduction

Glassy solids and related supercooled liquids have been the objects of studies of complex phenomena such as structural relaxation, glass transition, and crystallization.^{1,2} Among glass-forming substances, a group of organic compounds have attracted attention on account of their “fragility”³ in supercooled liquid states. As to the structural relaxation in organic glasses, results of thermal measurements on some compounds have been reported.^{4,5} However, almost no substantial structural information has been reported so far in relation to such a phenomenon.

We have recently studied the optical interference in film samples during their preparation by vapor deposition onto cold substrates and have found that the degradation in the interference pattern can be related to the density inhomogeneity in the sample.⁶ We have also found that the light scattering in the film can be used to detect structural changes in the sample due to the temperature elevation.⁷

The present paper reports the results related to these works, but this time, we concentrated our attention on the phenomena observed for transparent and homogeneous samples across their glass-transition temperatures. We carefully traced during the temperature elevation of vapor-deposited samples the intensity changes of the light transmitted through the samples. We found that the intensity changes observed before the light scattering by unknown causes starts to occur are attributed to the changes in the interference conditions, that is, the changes in the thickness and refractive index of the samples. Since the molecules used in our present study are considered to have molecular polarizabilities that are almost independent of the sample state, we can assume a simple relation represented by the Lorentz–Lorenz equation. By the use of this relation, we deduced the refractive indices and molar volumes of the samples. The results are quite informative, showing especially that the magnitude of the excess volume included in the initial sample at the vapor

deposition and the magnitude of the change in the sample volume due to the structural relaxation are both well related to the molecular structure of each compound. Thus, this work presents a new method for studying the structural character of molecular glasses. We report the above results in this paper and also discuss them in comparison with thermal data that have been reported for the structural relaxation in molecular glasses prepared similarly by vapor deposition.

2. Experimental Section

The source materials were purified by distillation and fractional crystallization. The vapor of each compound was introduced into a vacuum chamber and deposited on a gold-coated copper substrate mounted on a coldfinger (ST-400, Janis Research). The temperature of the substrate was controlled with a model 9650 temperature controller (Scientific Instruments) and was separately measured with a chromel–gold/iron(0.07%) thermocouple. The vacuum chamber (Figure 1) was designed for optical measurements on film samples that undergo glass transitions and attain fluidity in the supercooled liquid states. Thus, the substrate was held with its surface horizontal. Three optical ports were equipped respectively for introducing and monitoring the laser light and for measuring Raman spectra. The base pressure in the chamber was about 10^{-7} Pa.

Laser light from an Ar⁺ ion laser operated at 514.5 nm was introduced with s polarization with an angle of 60° from the normal of the substrate. The light reflected at the sample was monitored with a photodiode, and the intensity was recorded in a personal computer. As will be discussed later, this intensity is determined by the interference between the light reflected at the top surface of the sample and the light reflected at the sample–substrate interface. Hereafter, this light intensity will be called the transmission-light intensity for simplicity. The thickness of the samples was made to be about 10 μm by counting the number of the interference fringe of the transmitted light during the deposition of the vapor. After the deposition of the sample, its temperature was raised at a constant rate.

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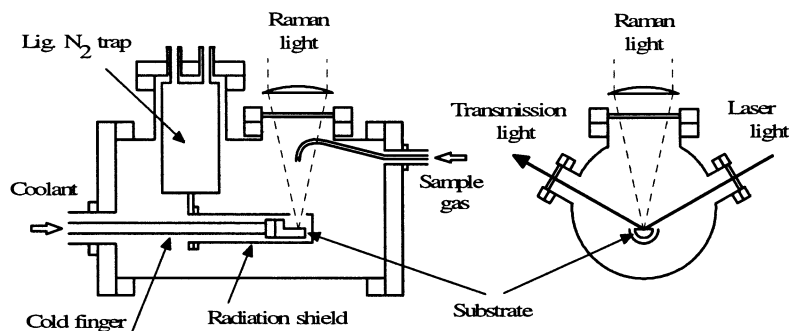


Figure 1. Construction of the vacuum chamber for the optical measurement on vapor-deposited glasses.

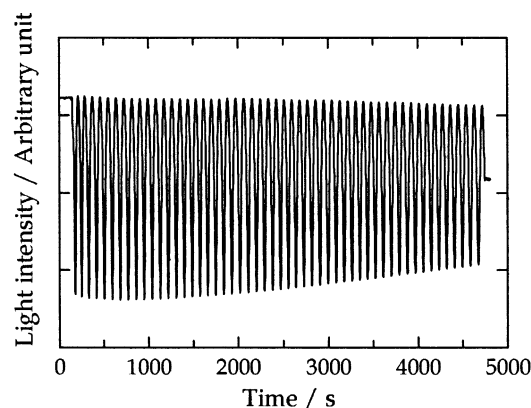


Figure 2. Example of the interference fringe of the transmitted light recorded during the vapor deposition of an ethylbenzene sample. As to the cause and shape of the dips, see the text.

The Raman light scattered from the sample to the vertical direction was used to confirm the sample material and also to monitor the final crystallization of the sample due to the temperature elevation. However, in the present work, we concentrated our attention on the intensity change of the transmission light since Raman spectra are rather insensitive to the structural change accompanying the glass transition in molecular glasses.⁸

3. Results and Discussion

3.1. Transmission-Light Intensity during the Deposition of Vapor and during the Temperature Elevation of the Deposited Sample. Figure 2 shows an example of the interference fringe recorded during the vapor deposition of an ethylbenzene sample. The dips in the light intensity are caused by the antiphase superposition of the light reflected at the top of the film sample and the light reflected at the film–substrate interface. The shape of the dips is well explained by an equation assuming multiple reflections of the light in the sample film,⁶ and the number of dips is related to the sample thickness if we assume a value of the refractive index of the film. We obtained similar interference fringes for toluene, ethylbenzene, and propylbenzene samples by vapor deposition at 78 K. The fact that the shape of the dips is kept even for up to 50 repetitions indicates the good transparency of the sample. The slight tendency of the shallowing of the dips is considered to arise from a slight degradation of the film surface and/or a slight inhomogeneity of the film thickness.

After the vapor deposition, we started the temperature elevation of the sample at a constant rate. Figure 3 shows a typical result of the change in the light intensity transmitted through an ethylbenzene film. This particular film was identical to that obtained by vapor deposition shown in Figure 2, the

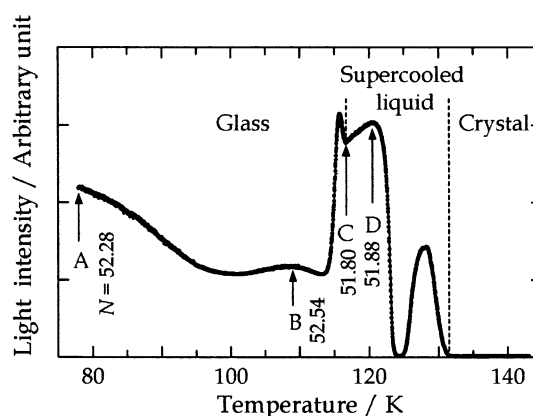


Figure 3. Evolution of the light intensity transmitted through the ethylbenzene sample that was prepared by the vapor deposition from which the procedure was recorded as the data in Figure 2. The symbols from A to D indicate the correspondence with particular points on the fringe during the temperature elevation at a rate of 0.36 K/min, and the numerical value beside each symbol is the value of the repetition number N of the fringe.

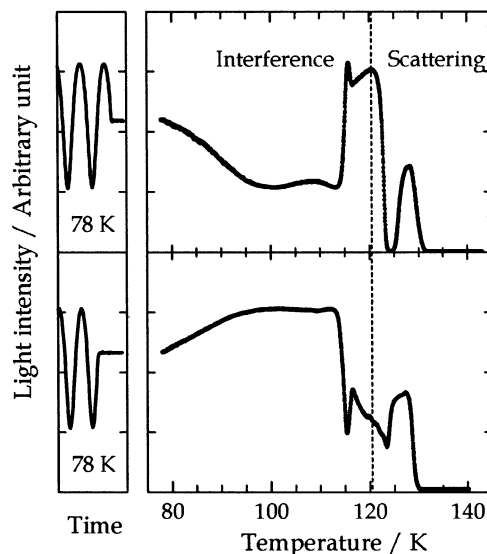


Figure 4. Comparison of the evolutions of the transmission-light intensity observed for ethylbenzene samples for which the vapor deposition was stopped at difference phases on the interference fringe. The data at the top are the same as in Figure 3.

deposition being stopped at the middle point of a dip where the light intensity was decreasing. As discussed next with the aid of Figure 4, the intensity change from point A to point D in Figure 3 is due to the change in the interference condition, and the change after point D is due to light scattering. Thus, from point A to point B, some change in the interference condition is considered to have caused a forward movement of the sample

state on the fringe. Hereafter, “forward” and “backward” mean respectively the directions of the increase and decrease in the phase of the fringe. The direction of the movement of the sample state then changed to backward at point B, and this backward movement continued until point C, where the movement changed to the forward direction again. These interpretations of the movements on the fringe will be confirmed later by comparing the analyzed data of the sample volume with the thermal expansion in the supercooled liquid state. The value of the fringe number N that corresponds to the phase of the repetition of the fringe was estimated from the transmission-light intensity. The results are indicated for the points from A to D in Figure 3 for this particular sample.

After point D, a dip in the light intensity was observed around 124 K. This is due to light scattering by an unknown cause,^{7,9} but we do not discuss this in detail in this paper. The sample finally lost its transparency around 130 K. This is due to the crystallization of the sample, since we observed a narrowing of the Raman bands in the same temperature region and also observed in separated experiments the appearance of Bragg peaks in X-ray diffraction patterns.⁷

As to the anomaly observed at point C (117 K), this is considered to arise from the glass transition, since the glass-transition temperature T_g of ethylbenzene has been reported to be 115 K¹⁰ (see also the discussion in section 3.3.). Thus, we can divide the temperature region shown in Figure 3 into three parts, namely, the glass, supercooled liquid, and crystal regions.

3.2. Confirmation of the Interference and Scattering Regions of Transmission-Light-Intensity Curves. As mentioned in the previous section, the transmission-light-intensity change between points A and D of the curve in Figure 3 is considered to arise from the change in the interference condition. If this is the case, then the shape of the light-intensity curve may be different when the vapor deposition is stopped at a different point on the interference fringe. We thus tried an experiment with an ethylbenzene sample for which the vapor deposition was stopped at a point on the fringe where the light intensity was increasing (the bottom curve in Figure 4). Obviously, the new curve shows features almost upside down in the region between 78 and 121 K compared with those for the previous sample (the top curve in Figure 4). This means that the forward and backward movements on the fringe during the temperature elevation were the same as for the previous sample between these temperatures. Therefore, the light-intensity change below 121 K shown in both the top and bottom parts in Figure 4 is considered to be brought about by the change in the interference condition.

Above 121 K, the new sample showed a small dip in the light intensity around 124 K and finally lost its intensity around 130 K. These changes are not due to the change in the interference condition but arise from the light scattering since we observed the enhancement of the scattered-light intensity.⁹ Note also that the changes above 121 K are almost in parallel with those in the top curve in Figure 4. The shape of the dip around 124 K depends on the sample, and the cause of this dip will be discussed elsewhere.⁹

3.3. Dependence of the Transmission-Light-Intensity Change on the Rate of Temperature Elevation. Since we raised the sample temperature continuously, the observed phenomena naturally depend on the rate of the temperature elevation. However, we found that this dependence is not serious. In Figure 5, we show the intensity changes of the light transmitted through three ethylbenzene samples during the temperature elevation at different rates. The features described

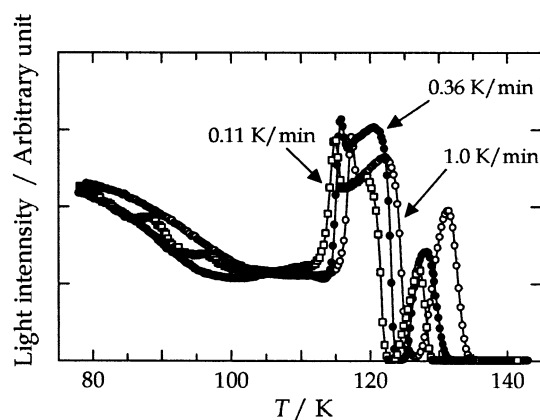


Figure 5. Comparison of the changes in the transmission-light intensity observed for ethylbenzene samples with different rates of temperature elevation.

for Figure 3 were almost reproduced in all of the experiments, although the temperature where each characteristic change was observed was shifted by several degrees. Thus, the intensity change of the transmitted light is considered to reflect the intrinsic temperature dependence of the sample properties. A small dip corresponding to point C in Figure 3 is seen at 116 K for the sample with a temperature elevation of 0.11 K/min. This temperature agrees well to T_g (115 K) determined by the calorimetric measurement with a much slower temperature elevation.¹⁰ The small undulations seen in the region from 85 to 100 K in the curve of 0.11 K/min were due to accidental fluctuations in the liquid-nitrogen flow in the coldfinger.

3.4. Relation of the State-Point Movement on the Interference Fringe to the Changes in the Refractive Index, Thickness, and Density of the Sample. On the assumption that the movement from point A to point D in Figure 3 is due to the change in the interference conditions, we tried to deduce the refractive index n , density ρ , and thickness d of the sample. Here, we first derive several equations relating these quantities to the repetition number N of the fringe.

From the difference in the light-path length between the light reflected at the top of the sample and the light reflected at the sample–substrate interface, the number of the fringe at a certain state of the sample is derived to be

$$N_0 = \frac{2d_0}{\lambda} \sqrt{n_0^2 - \sin^2 \theta} \quad (1)$$

where λ and θ are the wavelength and incident angle, respectively, of the laser light and the subscript zero is added to indicate that this state point on the fringe will be used as the origin in later calculations of various quantities. Even if the supply of the sample vapor had been stopped, the thickness and refractive index of the sample are changed by the temperature elevation. Let us suppose that the fringe number is increased by unity when the thickness and refractive index are changed respectively by Δd and Δn . Then, eq 1 may be changed to the form

$$N_0 + 1 = \frac{2(d_0 + \Delta d)}{\lambda} \sqrt{(n_0 + \Delta n)^2 - \sin^2 \theta} \quad (2)$$

Since there is no supply of the sample vapor, the change in the thickness is accompanied with a change in the density. We take into account here the fact that the sample is a thin film deposited on a substrate with a macroscopic size and also that the thermal-expansion coefficient may be larger for the organic

material than for the metal substrate. Then, the thermal expansion of the sample may not be necessarily three dimensional (3D). We thus represent Δd as

$$\Delta d = -k d_0 \frac{\Delta \rho}{\rho_0} \quad (3)$$

where ρ_0 is the density at the origin on the fringe, $\Delta \rho$ is the change in density, and k is a thermal-expansion parameter. $k = 1/3$ corresponds to 3D thermal expansion, and $k = 1$ corresponds to uniaxial thermal expansion.

We next assume the Lorentz–Lorenz equation that gives the relation between the density and refractive index, since the molecular polarizabilities of the compounds studied in this work may be considered to be constant in disordered states such as glass or liquid.¹¹ Namely,

$$R_M = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} \quad (4)$$

where R_M is the so-called molecular refraction and M is the molar mass. Then, by using eqs 3 and 4 and also the relation $\rho = \rho_0 + \Delta \rho$, we obtain the next equation of Δn from eqs 1 and 2.

$$\left\{ 1 + k - k \frac{(n_0 + \Delta n)^2 - 1}{(n_0 + \Delta n)^2 + 1} \frac{n_0^2 + 2}{n_0^2 - 2} \right\} \left\{ \frac{(n_0 + \Delta n)^2 - \sin^2 \theta}{n_0 - \sin^2 \theta} \right\}^{1/2} - \left(\frac{N_0 + 1}{N_0} \right) = 0 \quad (5)$$

We expand eq 5 into a polynomial of Δn and neglect the terms higher than quadratic. Thus, the left-hand side of eq 5 is reduced to the form

$$f(\Delta n, k) = a(k) \Delta n^2 + b(k) \Delta n + c(k) \quad (6)$$

where a , b , and c are complicated quantities containing k as a parameter. Before proceeding to the analysis of the fringe, we examine the properties of eq 6, paying attention to the relation between Δn and k .

Here, we again take the ethylbenzene sample in Figure 3 as the example. We calculated R_M to be 36.20 cm³/mol from the data of n and ρ at 293 K.^{12,13} We take point C (117 K) as the origin for calculating various quantities. By assuming that the temperature dependence of ρ reported for the region 160–320 K¹³ can be extrapolated to 117 K, we estimated n_0 at point C to be 1.615 using eq 4. Employing this and the values $N_0 = 51.8$ and $\theta = 60^\circ$, we calculated $f(\Delta n, k)$. The results are plotted against Δn in Figure 6 for various values of k . The solution of Δn is estimated in this diagram from the point $f(\Delta n, k) = 0$. Thus, for $k = 1$ (uniaxial expansion), Δn has two negative solutions. For k between 0.855 and 0.542, Δn is imaginary. For $k = 1/3$ (3D expansion), Δn has a positive solution and a negative solution.

The sample states between point C (the point of glass transition) and point D in Figure 3 are suitable for considering the properties of Δn since the sample is liquid between these points. As mentioned previously, the state point on the fringe moved forward by raising the temperature beyond point C. The sample volume may have been increased simultaneously by thermal expansion. As the volume increases, ρ decreases. The decrease in ρ causes a decrease in n if eq 4 is valid. Thus, a small forward movement on the fringe is accompanied by a decrease in n . Therefore, we first conclude that Δn is negative.

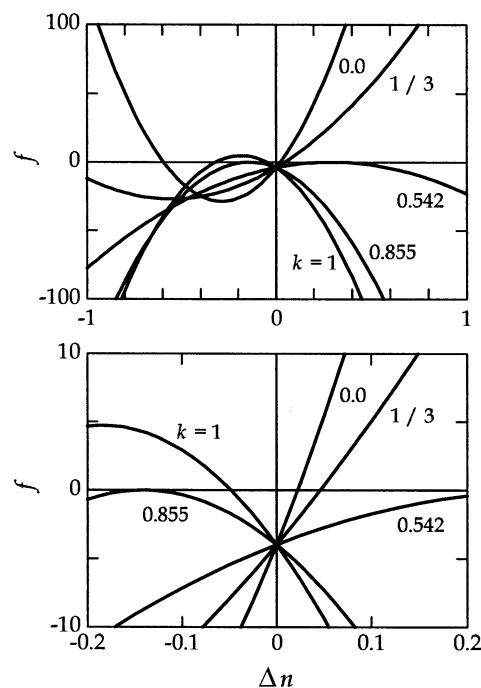


Figure 6. Plot of $f(\Delta n, k)$ against Δn with various values of the parameter k . The feature near the origin is magnified at the bottom. The solution of Δn is given from the point of $f = 0$. We can infer from these diagrams the allowed region of k in our samples (see the text).

TABLE 1: Principal Data in the Analyses of the Results for Three Compounds.

	n^a	$\rho/\text{g cm}^{-3}$ ^b	T_g/K	n_0^c	$\rho_0/\text{g cm}^{-3}$ ^d	Δn
toluene	1.505	0.866	117.2	1.623	1.030	−0.051
ethylbenzene	1.503	0.867	116.7	1.615	1.023	−0.048
propylbenzene	1.499	0.862	126.0	1.598	1.002	−0.045

^a Refractive indices at 514.5 nm estimated from the data at 293 K in ref 12. ^b Density data at 293 K from ref 13. ^{c,d} Estimated values at T_g (see the text).

In addition, it may be reasonable to assume that the absolute value of Δn is much smaller than unity since N_0 is much larger than unity. Then, we conclude that the region of the value allowed for k is between 0.855 and 1. In other words, the thermal expansion of our sample was almost uniaxial.

Hereafter, we assume that $k = 1$ since the uniaxial expansion is naturally expected for our sample geometry. Thus, the corresponding solution of Δn for an ethylbenzene sample is −0.048. The ambiguity accompanying Δn will be discussed later. Using such a value of Δn for each compound, we estimated for each point on the fringe by

$$n(T) = n_0 + \Delta n \{ \delta(T)/2\pi \} \quad (7)$$

where $\delta(T)$ was the phase difference on the fringe from point C and was estimated from the transmission-light intensity. The density and then the molar volume V_m were calculated by eq 4. The density and refractive index data around room temperature and the assumed n_0 and ρ_0 values (n and ρ , respectively, at T_g) are summarized in Table 1 for each compound along with Δn values for representative samples.

3.5. Results for Ethylbenzene. Figure 7 shows the evolutions of n and V_m of the ethylbenzene sample for which the change in the transmission-light intensity has been shown in Figure 3. We notice that V_m increases first as the temperature is raised until point B, where it starts an abrupt decrease to the value at

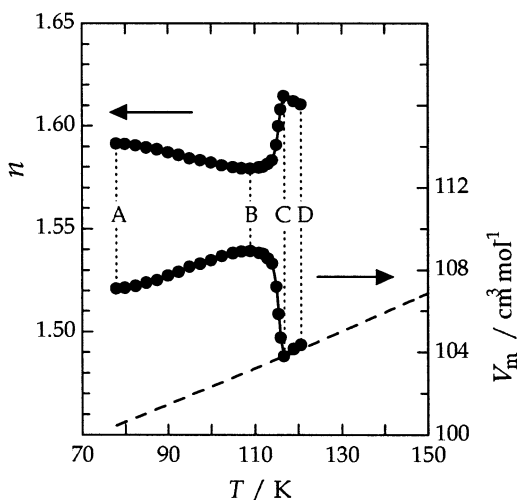


Figure 7. Changes in the refractive index n and molar volume V_m of an ethylbenzene sample for which the intensity change of the transmitted light is shown in Figure 3. The dashed line represents the extrapolation made in the preceding section that the solution of Δn is negative for the forward movement of the state point on the fringe in this temperature region.

point C. The initial increase in V_m is interpreted as the thermal expansion of the glass, and the abrupt decrease just below T_g is attributed to the structural relaxation. After the glass transition, V_m again shows an increasing tendency that is attributed to the thermal expansion of the supercooled liquid. This final fact is important in the present study since it supports the assumption made in the preceding section that the solution of Δn is negative for the forward movement of the state point on the fringe in this temperature region.

If we extrapolate the V_m curve of the liquid estimated from literature data to the temperature of the vapor deposition, then we obtain a value of about $100 \text{ cm}^3 \text{ mol}^{-1}$. Thus, the value of about $107 \text{ cm}^3 \text{ mol}^{-1}$ estimated for the initial glass state just after the vapor deposition was larger by 7% than that for the liquid at the same temperature.

It is roughly considered that the energy required for generating a void in a liquid is on the order of one-half of the energy for evaporating the corresponding number of molecules occupying the same volume.¹⁴ The enthalpy of vaporization of ethylbenzene is 42 kJ mol^{-1} at room temperature¹⁵ and is inferred to be a little larger than this value at low temperatures. We then roughly assume this value to be 50 kJ mol^{-1} in the supercooled liquid state. Thus, the above excess volume of 7% implies that the excess enthalpy of the initial ethylbenzene glass is on the order of 2 kJ mol^{-1} . This excess enthalpy is well compared with that estimated by thermal measurements for molecular glasses prepared by a similar method.^{4,5}

As to the value of the refractive index of the vapor-deposited molecular glass, substantial values were given by the present study for the first time. Thus, the value at the vapor deposition was smaller than the value at the glass-transition temperature but was larger than that of the liquid at room temperature. We must hereafter take into account this difference when we accurately estimate the sample thickness from the number of the fringe recorded during the vapor deposition.

3.6. Comparison of the Results for Toluene, Ethylbenzene, and Propylbenzene. In Figure 8, we compare the evolution of the volumes of toluene, ethylbenzene, and propylbenzene samples. In this Figure, the ordinate indicates the volume normalized by the value at T_g for each compound. Apparently, the excess volume at the initial vapor deposition is larger for the compound with the longer substituent on the phenyl ring. This is interpreted to mean that the void incorporated into the sample is larger

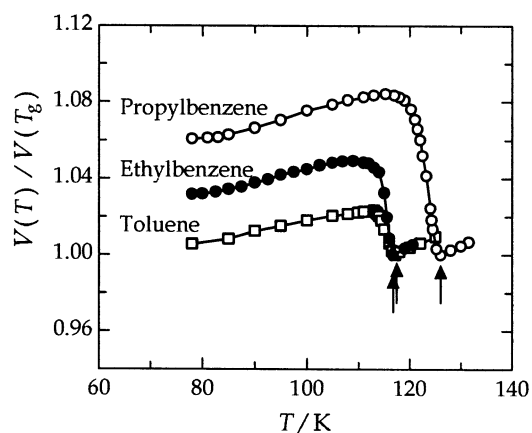


Figure 8. Comparison of the molar volume evolutions of the samples of three compounds. The ordinate indicates the volume normalized by the value at the glass transition of each sample. The arrows indicate T_g of each compound.

TABLE 2: Refractive Index and Molar Volume of the Glass State of Three Compounds at Vapor Deposition at 78 K

	n	$V_m / \text{cm}^3 \text{ mol}^{-1}$	$V_{m,\text{ex}} / V_{m,\text{liq}}$
toluene	1.618	89.9	0.04
ethylbenzene	1.591	107.1	0.07
propylbenzene	1.557	127.2	0.10

when molecules with longer substituents are deposited on the top surface of the sample in a disordered manner.¹⁶

Almost the same thing is mentioned as follows. The volume of the toluene sample at the vapor deposition was the same as that of the liquid at 124 K, 7 K higher than T_g . Such a temperature is sometimes called the fictive temperature when the energy or structure of the glass is compared with those of the liquid. Similarly, the fictive temperatures of the ethylbenzene and propylbenzene samples at the vapor deposition were estimated to be about 150 and 195 K, respectively. The differences between these fictive temperatures and T_g are considered to reflect the degree of disorder in the samples at the vapor deposition. Thus, the sample with the longer substituent initially has a more disordered structure. Table 2 summarizes the features of the glass samples prepared by vapor deposition at 78 K, where $V_{m,\text{liq}}$ is the molar volume of the supercooled liquid at the same temperature estimated by the extrapolation of the literature data¹³ and $V_{m,\text{ex}}$ is the difference between V_m and $V_{m,\text{liq}}$.

It has been reported that the fictive temperatures estimated by thermal measurements on glassy samples of butanenitrile and 1-pentene, which were prepared by vapor deposition at temperatures lower by about 30 K than their T_g 's, were higher by about 20 K than T_g .^{4,5} Thus, our toluene sample at the vapor deposition was not so disordered compared with these glasses, but the corresponding ethylbenzene and propylbenzene samples were much more disordered. These results may be ascribed to highly disordered intermolecular conformations of phenyl rings with long-chain substituents.

As to the width of the temperature range in which the structural relaxation of the glass was observed, there is also a correlation with the length of the alkyl substituents. Namely, the temperature intervals from the maximum point of the molar volume to T_g were 3.8, 8.0, and 10.6 K, respectively, for the toluene, ethylbenzene, and propylbenzene results in Figure 8. These temperature intervals are narrower than those observed for the enthalpy relaxations by thermal measurements.^{4,5} This is considered to arise from the rapid rate of temperature elevation in the present study. Anyway, the above results imply that the

structural relaxation of the glass with the longer substituent involves a larger number of steps in the conformational change and has a feature that resembles the structural relaxation in amorphous long-chain hydrocarbons such as $C_{24}H_{50}$. The relaxation in the latter amorphous materials takes place in very wide temperature ranges.^{17,18}

3.7. Several Comments. It was essential in the present study that the change in the transmission-light intensity due to the temperature elevation was related to the movement of the sample state on the interference fringe. The fact that transparent film samples were formed with good reproducibility made such an analysis possible. It was also essential that we could transform the glass samples into the supercooled liquid states for which the refractive index and density could be estimated by extrapolating the literature data. Thus, the present method cannot be applied to compounds in which the amorphous states undergo direct crystallization without manifesting the glass transition.

As to the final results shown in Figures 7 and 8 and Tables 1 and 2, we have a feeling that the absolute values of Δn might have been a little larger than the correct values since all of our V_m results show an inclination toward a larger thermal expansion of the supercooled liquid than the data extrapolated from the literature data. In the course of the analysis of the data, we made several assumptions or approximations; in short, (a) the Lorentz–Lorenz equation, (b) the neglect of the higher-order terms of Δn in eq 5, (c) $k = 1$, namely, the pure uniaxial thermal expansion, and (d) the extrapolation of the refractive index and density data of liquids to the low-temperature region. We have not yet made a detailed assessment of the errors brought about by these assumptions. However, the Lorentz–Lorenz equation is not considered to cause serious error in the present work if we refer to the extensive data accumulated by the classical analysis of molecular refractions and molecular polarizabilities.¹¹

As to the neglect of the higher-order terms of Δn , we confirmed that this causes an error in Δn of only about 1%. Similarly, the extrapolation of the refractive index and density data is not considered to bring about serious errors. As to the value of k , it might be a little smaller than unity. However, as shown in Figure 6, the absolute value of Δn increases if k decreases, which is contrary to the possible error in the estimation of the molar volumes described so far.

In conclusion, we observed light interference in films of three organic compounds during vapor deposition and temperature

elevation. We elucidated from the interference data the changes in the refractive index, density, and molar volume of the films due to the thermal expansion and structural relaxation in the glass state. This is the first report on the changes in these quantities for molecular glasses. The elucidated features are considered to be essential, although there remain small quantitative ambiguities in the results.

References and Notes

- (1) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. *J. Appl. Phys.* **2000**, *88*, 3113.
- (2) Debenedetti, P. G.; Stillinger, F. H. *Nature (London)* **2001**, *410*, 259.
- (3) Angell, C. A. *J. Phys. Chem. Solids* **1988**, *49*, 863.
- (4) Oguni, M.; Hikawa, H.; Suga, H. *Thermochim. Acta* **1990**, *158*, 143.
- (5) Takeda, K.; Yamamuro, O.; Suga, H. *J. Phys. Chem.* **1995**, *99*, 1602.
- (6) Ishii, K.; Yoshida, M.; Suzuki, K.; Sakurai, H.; Shimayama, T.; Nakayama, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 435.
- (7) Ishii, K.; Okamura, T.; Ishikawa, N.; Nakayama, H. *Chem. Lett.* **2001**, 52.
- (8) Ishii, K.; Nakayama, H.; Koyama, K.; Yokoyama, Y.; Ohashi, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2085.
- (9) Ishii, K.; Nakayama, H.; Okamura, T.; Ishikawa, K. To be submitted for publication.
- (10) Yamamuro, O.; Tsukushi, I.; Lindqvist, A.; Takahara, S.; Ishikawa, M.; Matsuo, T. *J. Phys. Chem. B* **1998**, *102*, 1605.
- (11) Le Fèvre, R. J. W. *Adv. Phys. Org. Chem.* **1965**, *3*, 1.
- (12) Wohlfarth, Ch.; Wohlfarth, B. In *Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology*; New Series, III/38B.; Lechner, M. D., Ed.; Springer: Berlin, 1996; Chapter 2.
- (13) Barlow, A. J.; Lamb, J.; Matheson, A. J. *Proc. R. Soc. London, Ser. A* **1966**, *292*, 322.
- (14) Tabor, A. J. *Gases, Liquids and Solids and Other States of Matter*, 3rd ed.; Cambridge University Press: Cambridge, U.K., 1991; Chapter 10.
- (15) *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1994; Chapter 6.
- (16) All of the film samples studied in the present work had good transparency since the interference fringes did not decay as shown in Figure 3, even after 50 repetitions. Therefore, the sample densities are considered to have been fairly homogeneous, and the void and disorder mentioned here are considered to be very small compared with the previously studied chlorobenzene films that were vapor deposited at very low temperatures.⁶ In the later cases, the films became opaque when the thickness was increased, indicating the appearance of density inhomogeneity the size of which may be comparable to the wavelength of light.
- (17) Hibino, Y.; Ishii, K.; Nakayama, H. *Mol. Cryst. Liq. Cryst.* **1990**, *187*, 175.
- (18) Ishii, K.; Nukaga, M.; Hibino, Y.; Hagiwara, S.; Nakayama, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1323.