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Structural relaxation of vapor-deposited molecular glasses and supercooled liquids

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Abstract

Molecular glasses prepared by vapor deposition have been revealed in recent years to have properties which the glasses prepared by ordinary liquid-quenching method do not have. Thus the vapor-deposition method of material preparation has attracted growing attention in the context of its possible application in manufacturing functional organic devices. The remarkable nature of vapor-deposited molecular glasses is that their properties depend very much on the deposition temperature and deposition rate. This suggests that the microscopic structure formed at the sample surface in the vapor deposition plays an important role in determining the sample properties. However, little of the structure of vapor-deposited molecular glasses has been clarified yet. In this article, we summarize first the research history of vapor-deposited molecular glasses, the concepts of amorphous solid and glass, and the methods for studying molecular glasses. We then summarize the research results reported to date for molecular glasses and related supercooled liquids. We also include in this article our recent research results in this field, and mention our present view on vapor-deposited molecular glasses.

1. Introduction

A glass is an amorphous solid which undergoes glass transition from a disordered solid state to a supercooled liquid (SCL) state in a narrow temperature region around the glass transition temperature (T_g) characteristic of the material.¹ A vast number of studies on glassy materials have been made from experimental and theoretical viewpoints including computer simulations,¹⁻¹⁰ but most of them took as the object the glasses prepared by liquid-quenching method and the related SCL states. Glasses are sometimes prepared by vapor deposition on to a cold solid surface, but the number of studies on such glasses is much smaller than those on the liquid-quenched glasses.

Studies on vapor-deposited molecular glasses were initiated by Seki and coworkers¹¹⁻¹³ in 1960's taking water and alcohols as the object using primitive apparatus for thermal measurements. By these studies, they confirmed glass transition phenomena of vapor-deposited molecular systems for the first time. About 20 years later, Suga and coworkers studied using an adiabatic calorimeter the relaxation enthalpy (H) of vapor-deposited butyronitrile¹⁴⁻¹⁶ and 1-pentene.^{16,17} They found that glass samples with H higher than that of liquid-quenched samples were formed with the deposition temperature (T_d) much lower than T_g . In these days, we were studying crystallization phenomena of vapor-deposited amorphous molecular systems,¹⁸⁻²³ and extended later the object to the compounds which undergo glass transition. In 2003, we contrived a practical method for estimating the change in the molar volume (V_m) of a vapor-deposited molecular sample,²⁴ and found that glassy samples of several alkylbenzenes deposited at T_d much lower than T_g of each compound exhibited relaxation accompanied with volume shrinkage in advance the glass transition.²⁴ These results qualitatively agreed with those reported by Suga and coworkers. The curve A in Fig. 1 schematically represents the structural relaxation with the decrease in H of such vapor-deposited glasses.²⁵

In 2007, however, Ediger and coworkers^{26,27} found that indomethacin (IMC) and tris-naphthyl-benzene (TNB) formed glasses with enthalpy lower than that of ordinary liquid-quenched glasses when the vapor-deposition was made at temperatures close to T_g . The curve B in Fig. 1 schematically represents the change in H of such vapor-deposited glasses. Since it was considered that glasses prepared by ordinary method should be annealed for a very long time to relax into such low-enthalpy states, these new glasses have sometimes been

called the ultra-stable glasses (USG). Although the conditions at the vapor deposition were different from those employed in the studies by Suga and coworkers¹⁴⁻¹⁷ and also by us,²⁴ the results obtained by Ediger and coworkers apparently contradicted the results obtained by the earlier studies. We thus examined the T_d dependence of V_m of samples of several alkylbenzenes.^{28,29} We found that V_m of as-deposited samples strongly depended on T_d , and the samples sometimes seemed to have V_m smaller than that of SCL of corresponding compound expected at the same temperature when T_d was close to T_g .

After such discoveries, a growing number of studies have been reported on the properties of vapor-deposited molecular glasses as described in the later parts of this article. On the other hand, the applications of molecular materials in the manufacture of molecular devices have been explored in the last several decades.³⁰⁻³² Lin et al.³³ found that the compounds used in organic light emitting diodes (OLED) formed glasses with anisotropic molecular orientation by vapor deposition. Yokoyama and coworkers³⁴⁻³⁸ found similar behaviors for many vapor-deposited organic materials and showed that such molecular orientations sometimes affect their properties. The basic studies of vapor-deposited molecular glasses are thus related to current researches in the field of technology.

In this article, we first describe the general concepts related to amorphous solids and glasses in section 2, and the methods for studying vapor-deposited molecular glasses in section 3. In section 4, we review the remarkable properties found so far for such glasses. In these reviews, we sometimes touch the properties of vapor-deposited amorphous molecular solids which do not exhibit glass transitions, since they have some properties common with those of glassy materials. Similarly, in section 5, we also touch some remarkable behaviors of SCLs made by heating vapor-deposited glasses through the glass transition temperature. This is because such behaviors are considered to manifest themselves by succeeding to the characteristics attained in the original glass states. In section 6, we report some of our new research results and discuss several issues related to molecular glasses. Finally in section 7, we make several concluding or supplemental remarks. For convenience, we list the symbols of quantities and abbreviations of samples states, methods and so on in Table. 1.

2. General concepts

Before proceeding to the topics of vapor-deposited molecular glasses, general and basic

concepts related to amorphous or glassy materials are described in this section. People who are familiar with such concepts can skip this section.

2.1. Amorphous solids and glasses

Solid materials with no periodic structure are called amorphous solids in general. Among them, those which undergo glass transition are called glasses.¹ Many amorphous solids made of neat compounds crystallize with temperature elevation in a range which is characteristic of each compound without passing through the SCL state. However, some of amorphous solids turn into SCL states with the temperature elevation in a range characteristic of the material. This is the glass transition. By rapidly lowering the temperature of SCL of such a material, an inverse state change into an amorphous solid occurs in almost the same temperature range. This inverse state change is also called the glass transition, and the characteristic temperature of the material is symbolized with T_g . If the temperature of a SCL which was made by heating a glass through T_g was heated further, the SCL usually crystallizes in a certain temperature range which is also characteristic of the compound. This is because the SCL state is metastable against the crystal state.

A glass state is considered to be a non-equilibrium state in which the disordered structure of SCL is frozen. On the other hand, a SCL state is usually considered to be an equilibrium state, although it is metastable with the free energy higher than the crystal state. However, in section 5 in this article, we briefly touch an issue of non-equilibrium nature observed for some of SCL states made by heating vapor-deposited glasses through T_g .

Many kinds of amorphous or glassy solids have been utilized in human life as typified by silicate glasses used as ordinary window glasses. In the second half of the twentieth century, in addition, many kinds of glassy materials made of organic polymers came to be used as structural materials, electric insulators, optical materials, and so on.^{39,40} As the examples of the inorganic and metallic amorphous materials, amorphous silicon¹ has come to be used in solar cells, and several kinds of amorphous metals⁴¹ are used, for instance, magnetic materials. Furthermore, organic glasses have recently come to be used in electric devices such as OLED.³³⁻³⁸ Currently, the use of organic glasses is expected to extend further to the field of solar cells and organic transistors.⁴² Thus, studies of organic glasses are increasing their importance.

Glasses sometimes categorized into several groups according to the nature of the chemical bonds forming them.¹ The groups and the typical examples are as follows: covalent glasses (SiO₂, As₂Se₃ etc.), ionic glasses (KNO₃-Ca(NO₃)₂, KCl-BiCl₃ etc.), metallic glasses (Zr-Cu, Ni-Nb etc.), van der Waals glasses (o-terphenyl, ethylcyclohexane etc.), and hydrogen-bond glasses (KHSO₄, ethanol etc.).

It has been also known that there is another viewpoint for investigating the nature of glasses. Interestingly, it is the temperature dependence of physical properties of the glass-forming SCL states such as dielectric relaxation time τ or viscosity η . Angell⁴³ pointed out that the compounds forming covalent glasses tend to exhibit a single Arrhenius behavior of τ or η in a wide range of temperature in the SCL state, while several organic compounds such as o-terphenyl and toluene exhibit a large deviation from the single Arrhenius behavior. Angell called the the former type SCLs strong glass-forming liquids and the latter type SCLs the fragile glass-forming liquids. Later, a parameter m defined by eqn (1) was proposed to characterize the property of a glass-forming SCL.⁴⁴

$$m = \left. \frac{d \log_{10} \langle \tau \rangle}{d(T_g/T)} \right|_{T=T_g} \quad (1)$$

m represents the steepness of the temperature dependence of the average relaxation time $\langle \tau \rangle$ of a SCL at T_g , and is called the steepness index or fragility index. Glasses formed from SCLs with larger m have been considered to have larger fragilities. Roughly saying, SCLs forming covalent glasses with network structures have small m , and SCLs forming molecular glasses made with van der Waals interactions have large m although its value scatters in a fairly wide range.

The deviation from the Arrhenius behavior was pointed out much earlier^{4,45-47} for the temperature dependence of η of low-temperature liquids. Eqn (2) is called the Vogel-Fulcher-Tammann (VFT) equation, and has been frequently assumed in expressing the behaviors of low-temperature liquids.

$$\log \eta = A + B/(T - T_0) \quad (2)$$

where A , B , and T_0 are the characteristic parameters for each compound. Recently, it was pointed out⁴⁸ that a more careful analysis of the temperature dependence of properties of SCLs should be made to evaluate m of glass-forming SCLs which are related to the vapor-deposited molecular glasses discussed in this article.

2.2 Glass forming processes

Molecular glasses are prepared in most of the cases with liquid-quenching or vapor-deposition methods, although a variety of methods are employed in the preparation of covalent, ionic, or metallic glasses.¹ As the temperature of a molecular liquid is lowered, its viscosity increases, and the translational and rotational thermal motions of the molecules are slowed down. Therefore, if a liquid was cooled with a sufficiently fast rate for avoiding crystallization, the sample would be frozen (come to be unable to change its structure toward the equilibrium structure) at T_g . This is the mechanism of glass formation with the liquid-quenching method. If a room-temperature liquid in a thin quartz tube was dipped into liquid nitrogen, the rate of cooling might be as large as 10^2 K/s.

On the other hand, in the vapor-deposition method, the source material is supplied with a vapor pressure much larger than the equilibrium vapor pressure of the material at the temperature of the substrate. The kinetic energy brought by a supplied molecule rapidly dissipates into the substrate or the frozen pile of the molecules. There is no conventional method to estimate the cooling rate in this process,¹ but it might be very fast if we assumed a temperature change of 10^2 K of the molecule within a short period of time which might be comparable to the rotational relaxation time of small molecules in a room-temperature liquid.⁴⁹ As a matter of fact, we can prepare glasses of compounds with small molecular sizes with the vapor-deposition method even if we cannot prepare them with the liquid-quenching method.

Structure of a glass is considered to depend in general on its preparation process. For example, it has been considered that structure of a liquid-quenched glass depends on the cooling rate.^{1,5} However, the actual T_g of a liquid-quenched molecular glass falls within a range of about 1 K around a temperature characteristic of the compound. In contrast, the apparent T_g of vapor-deposited molecular glasses of several compounds has recently found to exhibit an appreciable dependence on T_d . For example, T_g of vapor-deposited alkylbenzene glasses differs by a few kelvin depending on T_d ,²⁹ and in the case of TNB and IMC, magnitude of the difference could reach ten kelvin.²⁷ Interestingly, there are a few compounds of which T_g of their vapor-deposited glasses do not exhibit substantial T_d -dependence. Butyronitrile (BN) is an example of such compounds as described in section 6. T_g data of

representative vapor-deposited molecular glasses are listed in Table 2. For some of the compounds which are frequently referred to in this article, we indicate in this table the abbreviations of their names. We also included in this table T_{g0} which is T_g of liquid-quenched sample and T_{cryst} which is the crystallization temperature of SCL made by heating the vapor-deposited glass through the glass transition. We display the molecular structures of the representative compounds in Fig. 2.

2.3 Competition between direct crystallization and glass transition

An amorphous state of a neat substance generally comes upon a forked road when its temperature is raised. One is the way to direct crystallization and the other is the way to glass transition.⁵⁰⁻⁵² Note that the state changes along these ways are accompanied more or less with irreversible relaxation, since most of amorphous materials are in non-equilibrium states. In the cases of amorphous molecular samples prepared by vapor deposition, the degree of this non-equilibrium could be sometimes large. In general, compounds with rigid and/or symmetrical molecular structures tend to take the way to the direct crystallization, and compounds with flexible and/or asymmetrical molecular structures have a possibility to take the way to glass transition. We previously studied the competition between crystallization and glass transition for vapor-deposited chlorobenzene(CB)/toluene(TL) binary systems by changing the composition. Amorphous CB prefers direct crystallization, while TL prefers glass transition. Figure 3 summarizes the results in which the nature of CB seems to surpass that of TL, since a small amount of CB leads the whole system to crystallize.⁵² Table 3 lists the crystallization temperatures (T_{cryst}) of several molecular compounds for which the crystallization in their amorphous states were studied. T_{cryst} indicated with a range of temperature means that the corresponding compound crystallizes gradually or via several distinguishable steps when the sample temperature is continuously raised.

Besides the above issue of the crystallization of amorphous molecular solids, there are other interesting phenomena that some glasses forming molecular compounds exhibit crystal growth in the vicinity of T_g with rates much faster than those ordinarily observed in SCL states.⁵⁴⁻⁵⁷ These phenomena are considered to take place with the mechanism different from that of ordinary crystal growth in SCL states, since the rate of latter is slowed down with decreasing temperature towards T_g . Several mechanisms have been proposed⁵⁴⁻⁵⁹ for these

phenomena, but it seems that no definite answer has been obtained yet. We do not touch the details of these phenomena in this article.

3. Methods for studying vapor-deposited amorphous molecular systems

In this section, we describe the methods for studying the nature of vapor-deposited amorphous molecular systems. The substantial research results obtained with each method will be described in section 4. Although the temperature dependences of the properties of SCLs such as dielectric constants² and viscosity^{60,61} is sometimes important for the understanding of the nature of corresponding glasses, the methods for measuring these properties of SCLs are not touched in this article.

3.1 Sample preparations

There are several ways of vapor supply in the vapor-deposition method.¹ It is most easy, if the original material has a sufficient vapor pressure at room temperature. For example, the vapor evaporated from a liquid reserved in a room-temperature container can be introduced into a vacuum chamber and deposited on to a cold substrate. If the vapor pressure of the original material is not sufficiently large at room temperature, the material needs to be heated. Depending on the type of the original material, such sample heating is performed in various manners. For example, in the case of solid organic compounds with the molecular weight as large as several hundred, the powder material is filled in a container (crucible) and warmed with an electric heater.^{27,62} In our earlier studies on amorphous organic compounds,²² we fed the vapor by breaking in the vacuum chamber a thin glass tube, which contained the source material and was sealed with indium, to make the structure of the container simple. In the case of materials with a very high vaporization temperature, the vapor is sometimes formed with special techniques such as the sputtering method. In the case of the study of the vapor-deposited glass state of poly(methyl methacrylate) (PMMA), such a special technique was employed recently.⁶³ In any cases, it is important to monitor and control the rate of the vapor deposition and sample thickness, since these affect the nature of the sample.

Monitor of the sample thickness is usually made using a quartz crystal microbalance^{27,64-66} if the vapor pressure of the sample material is sufficiently small at room

temperature. It needs a special logic⁶⁶ to use the quartz crystal at temperatures different from room temperature. We used the light interference²⁴ in the film sample for estimating the thickness of the order of 10 μm . Ellipsometry^{62,67} may be important for the samples with the thickness less than the wavelength of visible light.

The vapor deposition of molecular compounds, for which their glass states are discussed in this article, is performed under rather mild conditions and has several merits from the viewpoints of the film-sample manufacturing as follows:³⁷ (1) good purity, (2) easy thickness control, (3) flatness of the top surface, (4) small effect of the substrate material. We describe below the structure of the vacuum chamber and attached piping system which we have used for the studies of the light-interference properties and Raman spectra of glasses made of small organic molecules.²⁴ We also describe briefly our sample-preparation process.

Figure 4 indicates the cross sections of the vacuum chamber. It was evacuated with a turbomolecular pump to the base pressure of 2×10^{-7} Pa. The substrate for the vapor deposition was a copper block plated with gold. It was attached to the head of a cold finger which was cooled with cold helium gas evaporating from liquid helium. This cooling method gave stability much better than the cooling with liquid nitrogen even in the temperature region higher than 80 K. The temperature of the cold finger was controlled with a Si-diode temperature sensor and an electric heater. The temperature of the copper block was separately measured with an Au-Fe/chromel thermocouple.

The sample vapor was introduced through a stainless piping system attached to the gas inlet of the chamber. The original liquid sample, purified by fractional crystallization, was contained in a glass tube connected to the piping system, and degassed in advance by several cycles of freeze and melt. The sample thickness was controlled by monitoring the interference fringe of laser light described in section 3.5.

As the substrate for the vapor deposition, different kinds of materials are employed according to the purpose of each study. As described above, we adopted a gold-plated copper block in the studies of light-interference and Raman scattering, a polished silicon single crystal in the study of X-ray diffraction, and a thin constantan plate in the DTA studies. In the studies by other workers, metallic sample pans were adopted for differential scanning calorimetry,²⁷ SiO_2 or Si plates for ellipsometry,³⁴⁻³⁶ SiO_2 plates for Brillouin scattering,⁶⁸ SiN_x films for AC-nanocalorimetry,^{65,66,69,70} and Al, Si, and V substrates for neutron scattering.^{26,64,71-73} In any cases, it should be remembered that the nature of the

vapor-deposited samples depends on the deposition rate and thickness, and also that it might be affected by the chemical and/or physical properties of the substrate material.

3.2 Thermal analyses

Thermal analyses are most important methods for studying glassy materials. At T_g , the heat capacity (C_p) of a material changes due to the change in the dynamic property of the constituent atoms or molecules, although the average or static structure of the material exhibits almost no appreciable change. In studying vapor-deposited molecular glasses, following several kinds of thermal methods have been employed; adiabatic calorimetry, quasi-adiabatic nanocalorimetry, differential scanning calorimetry (DSC), AC-nanocalorimetry, and differential thermal analysis (DTA).

Adiabatic calorimetry has been employed since the earlier studies of vapor-deposited molecular glasses,^{11,12,14-17,74,75} and informs us of precise values of heat capacity by repeatedly providing a known and small amount of heat and measuring the resultant temperature change. By this method, T_g is determined and information on enthalpy relaxation is obtained. However, a large amount of the sample, as large as 1 g, is needed in this method, and thus the vapor deposition takes a fairly long time to prepare the film sample of a sufficient amount. For example, in the study of Ramos et al. on EB, it took 96 h to prepare a 0.5 mm thick film on the inner surface of the sample container.⁷⁴

Quasi-adiabatic nanocalorimetry has been developed by Allen and coworkers,^{76,77} and uses a pair of film-shaped heat sensors made with SiN_x . The sample is deposited on one of the sensors and the other is used as the reference. The heat capacity of the sample is obtained by the analysis of the temperature difference between two sensors occurring due to the simultaneous application of a pulse-like electric current to the sensors. Measurements with this method can be performed with samples of thickness less than 100 nm. The calibration of the system is made using a material with the known heat capacity. Since the rate of temperature elevation in this method is very large, the characteristic temperature estimated for a state change of the sample is much higher than that obtained by other thermal methods. In the studies by Rodriguez and coworkers on TL and EB,⁷⁸⁻⁸⁰ the temperature of the 100 nm thick samples was raised by 3.3×10^4 K/s, and the estimated T_g s were about 30 K higher than the results of the adiabatic measurement⁷⁴ made with the rate of 0.67 mK/s.

The currently-used DSC is a method in which the heat flow to the sample is estimated from the temperature difference between the sample and reference placed symmetrically on a plate of the thermal sensor during the temperature elevation with a constant rate. In the original studies by Ediger and coworkers^{26,27} the sample was deposited in a vacuum on the surface of a metallic pan for the DCS measurement, and was moved in the atmosphere on to the DSC sensor. The sample thickness was 30–60 μm . This method can be applied to materials with T_g higher than room temperature and unaffected by atmosphere, especially by humidity.

AC nanocalorimetry is a modification of DSC, in which an alternate modulation is overlaid on the temperature elevation with a constant rate. It has a high sensitivity and can measure the heat capacity as well as the exothermic and endothermic changes. It has also a merit that it can monitor the change in the heat capacity at a quasi-constant temperature.^{81,82} Shick and coworkers⁶⁶ developed an apparatus for the in situ AC calorimetry for a vapor-deposited sample using a chip-form thermal sensor on which heaters and thermopiles based on a sub-micrometer SiN_x membrane were assembled. They applied this method to vapor-deposited samples of TL and EB⁶⁹, and IMC and TNB.^{65,70}

DTA is a primitive thermal method for studying a small amount of material, in which the temperature difference between the sample and reference is measured by raising the temperature with a constant rate. Seki and coworkers¹³ constructed a DTA apparatus in their earlier stage of the study of vapor-deposited molecular glasses. They made a DTA sensor with two constantan wires and copper plates soldered to a copper block to be cooled with liquid hydrogen. They studied using this apparatus the glass states of propene and chloroform. About 40 years after,⁸³ we invented a DTA sensor with which simultaneous measurements of DTA voltage and intensity of laser-light reflected from a sample film can be performed in a high vacuum chamber. The construction of the currently used DTA sensor made with a thin constantan plate and two chromel wires is displayed in Fig. 5. Attaching such a DTA sensor to a cold finger in a vacuum chamber, we studied thermal behavior of vapor-deposited EB^{83,84} as is described in section 4.3, and also the structural relaxation of high density alkylbenzene glasses as is described in section 6.

3.3 X-ray and neutron scatterings

While the small-angle X-ray scattering is sometimes used to study the inhomogeneity in amorphous solids and density fluctuation in liquids,¹ it has not yet been applied to the study of vapor-deposited molecular glasses. On the other hand, the wide-angle X-ray scattering (WAXS) has been used to see the amorphousness of molecular glasses. In the pioneering works by Bruneaux-Pouille and coworkers,^{85,86} they measured WAXS from TL in glass and liquid states and compared the results with those of crystals by referring to the radial distribution functions.

In our earlier studies⁸⁷ on amorphous molecular systems, we constructed an apparatus with which in situ WAXS measurements on vapor-deposited samples can be performed down to 13 K simultaneously monitoring laser-light reflection from the sample. A gold-plated copper block or a plate of silicon single crystal was used as the substrate. Using this apparatus, we studied the direct crystallization processes of amorphous benzene⁸⁷ and halogen mono-substituted benzenes.⁸⁸⁻⁹⁰ We also studied the anomaly in the SCL state of EB,⁹¹ and the competition between the crystallization and glass transition of binary systems of TL or EB with chlorobenzene (CB).^{52,92}

After the discovery of the vapor-deposited USG of IMC and TNB, Ediger and coworkers^{93,94} obtained broad amorphous patterns by the ex situ WAXS measurements on these glasses, and examined anisotropy and structural change with time. For IMC,⁹³ they obtained a two-dimensional diffraction pattern with a grazing incidence angle. Recently, we studied in situ the changes in the broad amorphous patterns of several alkylbenzene glasses around T_g .⁹⁵ This will be described again in section 6.

In the case of the neutron scattering, experiments are performed with both elastic and inelastic conditions. Ediger and coworkers^{26,64,71} made ex situ measurements on laminated samples of TNB and deuterated TNB, and estimated the diffusion coefficient of the molecule from the intensity change of the Bragg peaks. Yamamuro and coworkers constructed a cryostat for the in situ neutron scattering experiments on vapor-deposited molecular glasses.⁷² They performed the elastic and inelastic scattering experiments on glass states of CS₂⁷³ and H₂O.^{72,96} They studied the structural characteristics and the low-energy excitation band called boson peak which is sometimes observed for amorphous materials.

3.4 Raman and Brillouin scatterings

Raman scattering is widely used to study molecular vibrations in various states and optical phonons in solid materials. On the other hand, Brillouin scattering is a name of the light scattering method to see acoustic phonons in materials. The basic mechanisms of these two light scatterings are similar to each other. However, the magnitude of the wavenumber shift of scattered light from the excitation light is much smaller in Brillouin scattering than in Raman scattering. Thus a Fabry-Perot type interferometer is usually employed to observe Brillouin scattering in place of an ordinary grating spectrometer used to measure Raman scattering.

For molecular compounds of which the molecular structure does not depend largely on the sample state, Raman spectra in the region of *intra*-molecular vibrations do not depend so much on the state. However, spectra of *inter*-molecular vibrations observed in small wavenumber regions strongly depend on the structural order of the sample. In our earlier studies on amorphous molecular systems, we measured such small-wavenumber Raman spectra of vapor-deposited aromatic hydrocarbons.^{21,22,87}

Using Raman spectra of *intra*-molecular vibrations, we studied^{18,23} the multi-stage crystallization processes of amorphous linear hydrocarbons in combination with infrared absorption spectra. We also studied the conformational transformation and crystallization in amorphous 1,2-dichloroethane⁹⁷ and biphenyl.^{19,20} All the compounds mentioned here have characteristic freedom of molecular deformation, and exhibit appreciable changes in *intra*-molecular vibrational spectra especially at crystallization. Thus Raman scattering is useful in studying their structural change accompanying the crystallization. Some results obtained by such studies will be described in section 4.5.

In contrast to the case of crystallization, it is difficult to detect glass transition with Raman scattering, since almost no change in the average molecular environment takes place at T_g . We barely recognized the glass transition of butyronitrile⁹⁸ by precisely analyzing the temperature dependence of the wavenumber of a Raman band. We also recognized the glass transition of propyl alcohol by analyzing the temperature dependence of the intensity ratio of two Raman bands which were attributed to different conformational isomers.⁹⁹ These fortunate recognitions of glass transitions are considered to be led by the change in the direction of volume change at glass transition; that is, the volume shrinkage due to the structural relaxation in the vapor-deposited glass state as approaching T_g and the thermal expansion in the SCL state above T_g .

With the method of Brillouin scattering, one can obtain the information on mechanical

properties of the material such as sound velocity and elastic modulus through the measurement of acoustic phonons. Ediger and coworkers applied this method to IMC and TNB samples deposited on a SiO₂ substrate.^{68,100}

3.5 Refractive index (ellipsometry and light interference)

Ellipsometry is generally used in the study of thin films made on solid substrates. In this method, the change in the polarization of incident light due to the reflection at the sample is measured, and the refractive index and thickness of the film are estimated through a calculation based on an optical model of the film and substrate. Practically, several different setups of the measurement are used as this method.⁶⁷ Lin and coworkers³³ estimated the complex refractive indices of vapor-deposited films of ter(9,9-diarylfuorene)s which is a material used for manufacturing OLED. Yokoyama and coworkers³⁴⁻³⁸ estimated the refractive indices of more than ten materials for OLED manufacturing in glass states. Ediger and coworkers performed ellipsometry on vapor-deposited films of IMC^{62,101} and TNB.¹⁰²

Ellipsometry is rather difficult to be performed in situ for low-temperature samples in a high vacuum, although such conditions are required to study vapor-deposited samples of compounds with small molecular sizes. We therefore contrived a simple method²⁴ to estimate the changes in the thickness and refractive index of a film deposited on a metallic substrate due to the temperature elevation. This method is based on the interference of laser light in the film. First, we record the periodic change of the reflected-light intensity during the vapor deposition at a constant temperature. After stopping the deposition, we start the temperature elevation with a constant rate by continuing the record of the reflected light intensity. At this stage, the light intensity exhibits a rather slow change due to the gradual changes in the thickness and refractive index of the sample. Such a change in the reflected light intensity shows a pattern characteristic to the state change exhibited by the material. Thus by the analysis of the pattern, we can elucidate the change in the thickness and refractive index of the sample due to the temperature elevation.

In the above analysis, we made several expedient assumptions²⁴ on the structure and optical response of the sample. However, as it will be discussed in sections 5 and 6, we have found characteristic changes in the properties of several kinds of molecular glasses using the above interference method.^{24,28,29,103,104} We thus believe that the results obtained with the

above interference method are valid, if we make allowance for the semi-quantitative nature of the method. Unfortunately, this method cannot be applied to the samples with which the periodic change in the reflected light intensity during the vapor deposition is diminished seriously due to the appearance of optical inhomogeneity in the sample.

3.6 Other methods (SIMS and computer simulations)

There is an experimental method called SIMS (secondary ion mass spectrometry) for studying the chemical composition at the surface of solid materials.¹⁰⁵ In this method, accelerated atomic or molecular ions hit the surface of the sample, and the chemical species emitted as the secondary ions are analyzed with mass spectroscopy. One can know thus the chemical species existing at the surface of the sample. Ediger and coworkers¹⁰⁶⁻¹⁰⁹ examined with SIMS the composition, as a function of the depth from the top surface, of the vapor-deposited samples which were prepared by the alternative vapor depositions of normal and deuterium-substituted compounds of IMC or TNB. From such studies, they estimated the diffusion coefficient of the molecule in glass samples. Souda¹¹⁰⁻¹¹⁴ also studied the surface state of vapor-deposited molecular glasses by SIMS. He made about one molecular layer of a deuterated compound on the top of a vapor-deposited glass of an ordinary compound. He analyzed the composition at the sample surface by raising the temperature. He examined glasses of alkylbenzenes, 3-methylpentane, 1-pentene, and several alcohols.

As well as the experimental methods described so far, computer simulations also play their roles in the studies of glasses. However, the number of studies made on vapor-deposited molecular systems is rather small compared with the wide variety of studies made on liquid-quenched glasses or SCLs.¹¹⁵ Singh and de Pablo¹¹⁶ virtually constructed vapor-deposited glasses and SCLs of trehalose by a molecular dynamics (MD) simulation. de Pablo and coworkers^{117,118} performed similar simulations for vapor-deposited glasses of binary Lennard-Jones particles. Harrowell and coworkers^{119,120} performed simulations on three-dimensional systems of two-state spins. Several results obtained by such simulations will be described in section 4.

In a similar way to MD simulations, quantum-chemical calculations on molecular systems can be used to explore the microscopic structures in molecular glasses. As a start of such exploration, we tried calculations¹⁰⁴ to see the manner of dimer formation of

alkylbenzenes with the Gaussian09 package.¹²¹ Although a number of quantum chemical calculations have been performed to see the stable structures of molecular clusters,¹²²⁻¹²⁷ it has been difficult to obtain a sufficient data for a variety of locally stable structures made of glass-forming flexible molecules. We will touch briefly in section 6 a trial in this relation.

From the viewpoint of the application of vapor-deposited molecular glasses, studies of their electronic states may be important. Properties related to the electric conduction may also be interested, and studied actively for the materials used in device manufacturing. However, we are not surveying literatures in these fields.

4. Properties of vapor-deposited molecular glasses

In this section, we summarize the properties of vapor-deposited molecular glasses by referring to the leading literatures we have noticed so far.

4.1 Influences of conditions in sample preparation or annealing

Properties of vapor-deposited molecular glasses depend on T_d , rate of deposition (v_d), sample thickness, and so on. Since the effect of T_d is the most remarkable among these, we discuss it throughout this section. Therefore, we touch mainly in this first section the effects of others.

It was reported¹²⁸ that H and the fictive temperature (T_f), which are sometimes used for discussing stability of glasses (see the next section), of USG of IMC and TNB were lower as v_d was slower. We recently obtained the related data about the v_d dependence of density for EB glasses, and will discuss the results in section 6.

For glassy polymer films, T_g has been known to depend on the thickness.^{129,130} Similarly, for vapor-deposited TL glasses, the onset temperature ($T_{g,on}$) of the glass transition and T_f depended on the thickness when they were thinner than about 30 nm.^{131,132} When the thickness of USG of IMC was smaller than 1 μm , the relaxation time to the SCL states at temperatures slightly above T_g was smaller as the thickness was smaller, but it was almost independent of thickness when the thickness was larger than 1 μm .⁷⁰

There have been many experimental findings that the nature of the substrate material does not give remarkable effect to the property of vapor-deposited glasses. Yokoyama and coworkers^{35,37} obtained glasses of compounds used for OLED manufacturing by the

deposition on to the substrate of Si, Ag, ITO (In/Ti oxide), or organic films. They found that all the samples had structures in which the long molecular axis oriented parallel to the substrate. Ediger and coworkers²⁷ found that C_p and T_f of the glasses of IMC deposited on the substrate of Al, Cu, or a polycarbonate film did not exhibit appreciable difference.

Impurities affect, of course, the properties of glasses. Ediger and coworkers¹⁰⁹ reported that contamination coming from the vacuum-pump oil affected the molecular diffusion velocity in SCLs obtained through the glass transition of IMC or TNB. In the case of the sample material with a large hydrophilicity, especially if the sample is treated in the atmosphere, one should also be careful about humidity.

Since glasses are in non-equilibrium states, they exhibit structural relaxation with time in general and their properties change slowly. Thus the apparent T_g determined by raising the temperature continuously depends on the rate of the temperature elevation.²⁴ Similarly, deeply supercooled liquids sometimes have very long relaxation times, and thus the phenomena observed for SCLs also depend on the rate of the temperature elevation.

4.2 Thermal properties

Thermal properties of vapor-deposited glasses such as C_p or H depend remarkably on T_d . Glasses thermodynamically or kinetically more stable than ordinary liquid-quenched glasses were formed with several organic compounds by vapor deposition at T_d close to their T_g . The thermodynamic stabilities of such glasses are sometimes discussed⁷⁴ using T_f defined as the temperature where two curves cross each other: one is the curve of the temperature dependence of H of the glass and the other is the extension curve of the temperature dependence of H of SCL. On the other hand, the kinetic stabilities are discussed usually using $T_{g,on}$ or T_g itself.

Hereafter, we indicate the temperature data such as T_d in each experiment with the value relative to the glass-transition temperature (T_{g0}) observed for the ordinary liquid-quenched glass of the compound. We also use the same symbol when we refer to the T_g data mentioned in literature without indicating the method of T_g determination.

As to the glasses of IMC and TNB, studies with DSC and AC nanocalorimetry have been performed.^{26,27,65,70,133} Among IMC glasses deposited at T_d in the range of $0.6T_{g0} \sim T_{g0}$, the sample prepared at $0.85T_{g0}$ exhibited the lowest T_f , that is, it had the lowest H . In addition, its

C_p was smaller by 4.5% than a liquid-quenched glass.¹³³ For TNB, the deposition at $0.85T_{g0}$ also gave a thermodynamically and kinetically stable glass, and its C_p was smaller by about 4% than a liquid-quenched glass.⁶⁵

As to the glasses of EB, adiabatic calorimetry⁶⁸ indicated that the enthalpy curve was located below that of liquid-quenched glass when T_d was in the range of $0.79T_{g0} \sim 0.96T_{g0}$. The apparent T_g was the highest for the glass with T_d of $0.92T_{g0}$, and T_f was the lowest for the same glass. With the AC-calorimetry,⁶⁹ the glasses with T_d in the range of $0.75T_{g0} \sim 0.96T_{g0}$ exhibited C_p smaller by 2 ~ 4% than the liquid-quenched glass, and kept the glass state up to higher temperatures than T_{g0} . The AC-calorimetry gave similar results to TL glasses.⁶⁹

The quasi-adiabatic nanocalorimetry,⁸⁰ in which the sample thickness was thin (~ 100 nm) and the rate of the temperature elevation was very large, gave the lowest T_f of TL and EB glasses for the samples with T_d of $0.8T_{g0}$, and the same samples kept the glass states to the highest T_g .

Although the thermal sensitivity was small in the DTA experiments, the simultaneous observation of DTA and the light interference indicated^{83,84} that the high density EB glasses exhibited heat absorption preceding the glass transition in agreement with the results of the adiabatic calorimetry.⁷⁴ This result ascertained that the anomalously dense glasses were simultaneously low enthalpy.

For BN^{14,15,17} and 1-pentene^{16,17} studied in the pioneering works, it was found that H of as-deposited samples of these compounds was higher than those of the liquid-quenched glasses when T_d was sufficiently lower than their T_{g0} . As it will be discussed in section 4.3, these compounds may not form glasses with anomalously low H . Finally the MD simulation, in which trehalose¹¹⁶ or two components Lennard-Jones particles^{117,118} were taken as the model molecules, indicated that the vapor-deposited glasses could have an energy lower than liquid-quenched glasses.

4.3 Density or molar volume

The densities of vapor-deposited glasses remarkably depend on T_d , just like the thermal properties. For some compounds, glasses with high densities are obtained when T_d is close to T_g of the compound.

By the light-interference method contrived by us,²⁴ changes in V_m of alkylbenzenes due

to the temperature elevation have been estimated for glasses prepared with different T_d . Figure 6 indicates the results for TL.²⁹ The horizontal axis represents the temperature normalized by T_{g0} , and the vertical axis represents V_m normalized by the value expected for SCL at T_{g0} . The dashed line represents the extension of the temperature dependence of V_m of TL liquid. It is seen that V_m in the initial state just after the deposition was larger as T_d was lower except the T_d region close to T_g . These results suggest that the glasses deposited at sufficiently low T_d involved a large excess volume or voids in the disordered structure. Such disordered structures of glassy or amorphous molecular solids are considered to comprise molecular clusters with a wide range of size. The size of larger clusters is considered to approach sometimes the order of the wavelength of visible light, because the samples tend to lose transparency if T_d was too low.⁸⁹

With the temperature elevation after the deposition, TL glasses with larger V_m exhibit thermal expansion initially and then exhibit shrinkage as the temperature approaches T_g . On the other hand, the samples with V_m value comparable to or smaller than that of SCL exhibit a sudden expansion at a temperature just below T_g . There is a clear tendency that T_g of each sample is higher as the initial V_m is smaller. Thus, the smallness of the initial volume of vapor-deposited glasses may be related to their kinetic stability.

For the glasses of EB, PB, and IPB,²⁹ the T_d -dependences of V_m were similar to the case of TL, although the minimum value of the initial V_m was observed at T_d around $0.9T_{g0}$ for EB, PB, and IPB while that was observed at T_d around $0.95T_{g0}$ for TL. The thermodynamically and kinetically stable glasses of EB were found to form also at around $0.9T_{g0}$ by the thermal measurements.^{74,133}

The earliest information on the density of TNB glasses²⁶ was obtained by X-ray reflection. Afterwards, the density information was obtained for IMC and TNB glasses by ellipsometry.^{62,101,102} In the case of IMC, the ellipsometry was performed for the samples with T_d from $0.67T_{g0}$ to the vicinity of T_{g0} . The results indicated that the initial density took the maximum value at T_d around $0.85T_{g0}$ and was larger by about 1.4% than the density of a liquid-quenched glass. This sample had also the highest $T_{g,on}$. For TNB, results of ellipsometry similar to those for IMC were obtained, although the number of the examined T_d was smaller. For the sample with T_d of $0.85T_{g0}$, the density was larger by 1.3%¹⁰² or 1.7%²⁶ than that of SCL.

In summary of the above description on the densities of several vapor-deposited glasses,

IMC and TNB form glasses with densities larger than those of liquid-quenched glasses. In the cases of alkylbenzenes, the results were presented with V_m and indicated that they form glasses with densities larger than the value expected for the SCL state of each compound at the same temperature. It was also found by computer simulations¹¹⁶ that trehalose forms high-density glass by vapor deposition. However, formation of such high-density glasses cannot be expected for every organic compound. In Fig. 7, the T_d -dependence of V_m of the as-deposited glasses of alkylbenzenes are summarized as well as those of ECH and BN. The horizontal and vertical axes represent T_d and V_m , respectively, normalized by the same manner as in Fig. 6. The solid lines are guides for the eyes to indicate the T_d -dependence of V_m of the as-deposited glasses. The dashed lines indicate the extension of the temperature dependence of V_m of each compound in the liquid state. We previously defined¹⁰⁴ the temperature (T_i) of each compound as the temperature of the cross point between the solid and dashed lines. Figure 7 indicates that each compound has a possibility to form glasses with the density larger than that of SCL at the same temperature with T_d between T_i and T_{g0} . In the cases of alkylbenzenes, the temperature interval between T_i and T_{g0} is wide, but in the cases of BN, the mutual relation between T_i and T_{g0} is inverted. Thus BN is considered to have no possibility to form dense glasses. Figure 7 also indicates that ECH has a slight possibility for the formation of dense glasses and an intermediate property between the alkylbenzenes and the group of BN.

4.4 Molecular motions or diffusion

It has been found, for glasses made of either small molecular-weight compounds or polymers,⁹ that the molecular diffusion at the free surface is faster than that in the bulk. Zhu et al.¹³⁴ studied with the atomic-force microscope the degradation of the corrugated surface of a liquid-quenched glass of IMC, and found that the molecular diffusion at the surface was faster than in the bulk by 10^6 times in the vicinity of T_g . For vapor-deposited glasses, the following results have been reported about the molecular diffusion.

Ediger and coworkers^{26,27} studied the molecular diffusion at the phase boundary between TNB and deuterated TNB by neutron diffraction. From the results, they estimated the structural relaxation time at the top surface of TNB during the vapor deposition at $0.85T_{g0}$ to be a few second. In comparison, the relaxation time in the bulk TNB at the same temperature

was estimated to be 10^2 years.¹³⁵

Ediger and coworkers¹⁰⁶⁻¹⁰⁹ studied also the transformation process from glass to SCL by SIMS. They found for USG ($T_d = 0.85T_{g0}$) of TNB and IMC¹⁰⁷⁻¹⁰⁹ that the transformation started at the free surface and proceeded into the bulk making a growth front when the samples were annealed at a temperature slightly higher than their T_{g0} . On the other hand, in the glasses deposited at a temperature very close to T_g ($T_d = 0.98T_{g0}$),^{106,107} the transformation occurred almost homogeneously in the bulk. They explained the mechanism of the transformation of USG accompanied with the growth front by the necessity of the contact with the molten phase to initiate the transformation even at a temperature above T_g .

As to the molecular diffusion in alkylbenzene glasses, Souda¹¹⁰⁻¹¹² found with SIMS that the molecular diffusion at the surfaces of TL, EB, and IPB glasses starts to increase at a certain temperature below T_g , and this temperature was lower as T_d was lower. He also studied similar phenomena for vapor-deposited methanol, ethanol, and 1-propanol glasses, and detected for methanol¹¹³ an enhancement of molecular diffusion at the surface at temperature much lower than T_g .

MD simulation gives also the information on the molecular motion in vapor-deposited glasses. It was found using trehalose as the model compound¹¹⁶ that the Debye-Waller factor $\langle u^2 \rangle$ of the molecules at the top surface of sample, where u stands for the thermal displacement of the molecule from its equilibrium position in the direction normal to the substrate, was larger by several hundred than that of the molecules in the bulk. The simulation with a binary system of Lennard-Jones particles¹¹⁸ indicated that the increase in $\langle u^2 \rangle$ developed from the surface into the bulk when the sample was annealed at a temperature close to T_g , although similar simulation with a liquid-quenched sample exhibited the uniform increase in the whole sample. In addition, the larger relaxation rate of molecules at the surface than that in the bulk and the development of the relaxation phenomena from the surface to the bulk were observed in the simulation with a system with two spin states.¹¹⁹

In summary of these findings on molecular motions or diffusion in vapor-deposited glasses, (1) the diffusion at the surface was faster than in the bulk, (2) the glass transition of a USG ($T_d = 0.85T_{g0}$) took place developing from the surface into the bulk in contrast to the behavior of the glass deposited at a temperature in the very vicinity of T_{g0} , (3) the enhancement of surface diffusion was observed for alkylbenzene glasses prepared at low T_d s when the temperature was raised approaching T_g . The above second point suggests that USG

incorporates locally stable intermolecular conformations which ordinary liquid-quenched glasses do not comprise. The third point is also interesting because the alkylbenzene glasses prepared at sufficiently low T_d are considered to undergo structural relaxation prior to the glass transition as observed in the evolution of their molar volume.²⁹

4.5 Locally stable aggregation

As it was described in the previous section, the existence of locally stable molecular packing is suggested by the slow molecular diffusion in the bulk of USG. Similar structural characteristics have been considered for the formation of the dense glasses of alkylbenzenes.²⁹ However, we have obtained little information until now about the molecular packing in vapor-deposited glasses.

In our early studies on vapor-deposited amorphous anthracene,²¹ we observed curious Raman bands in the lattice-vibration region. These bands suggested that molecular pairs with a strong intermolecular interaction, not existing in the crystal state, were formed in disordered samples when the deposition was made in a temperature range of medium T_d . Interestingly, the crystallization temperature of the amorphous samples with these bands was higher than that of the samples without such Raman bands. In the case of amorphous 1,2-dichloroethane,⁹⁷ the amount of gauche molecules, which are stable in the liquid state, gradually increased with the temperature elevation of samples deposited at sufficiently low T_d . However, the samples deposited in a temperature range of medium T_d exhibited an appreciable delay in the increase of gauche molecules. This suggests the effect of some locally stable conformations in the sample deposited at medium T_d .

On the basis of the above experiences, we infer that locally stable intermolecular conformations could be formed in the vapor-deposition processes of molecular compounds. Naturally, the probability of the formation of such conformations should depend on the molecular structure as well as the substrate temperature and deposition rate. We thus performed, as a starting trial, quantum chemical calculations on the dimer of several alkylbenzenes, ECH, and BN¹⁰⁴ using the Gaussian09 package software.¹²¹ With these calculations, it was found first that the interaction between the π -electron system of the phenyl ring and a C-H bond in the alkyl substituent is important in the alkylbenzene dimers. This might cause the formation of locally stable intermolecular conformations in the dense glasses.

Secondly, the intermolecular interaction between BN molecules was found to be strong although BN exhibits no sign of formation of dense glasses. We thus considered¹⁰⁴ that the large dipole moments of BN molecules make so strong dimers that the resultant dimers might behave as non-polar molecular units.

4.6 Anisotropy of glasses

A large number of studies have been made on the molecular orientation and/or anisotropy in vapor-deposited molecular films,¹³⁶ but most of these concern crystalline films. As to the anisotropy of vapor-deposited glasses, a few studies have been made with ellipsometry, WAXS measurements, and MD simulations.

According to the measurements of complex refractive indices with ellipsometry on oligomers of 9,9-diarylfuorene,³³ the π - π^* electronic transition moment and thus the long molecular axis has a tendency to lie parallel to the substrate. Similar measurements by Yokoyama and coworkers³⁴⁻³⁷ on several compounds used in OLED manufacturing indicated that the tendency to form anisotropic films was larger with the compounds with larger anisotropy in the molecular structure, and in most of the cases, the long molecular axis lied parallel to the substrate. They also found, for the samples deposited in the T_d region from $0.7T_{g0}$ to a temperature just below T_{g0} , that the tendency was larger with lower T_d .

Ediger and coworkers^{62,101} indicated that the birefringence of IMC glasses depends on T_d . For the glasses prepared at T_d around $0.9T_{g0}$, n_z was larger than n_{xy} , where n_z and n_{xy} stand for the refractive indices perpendicular to and parallel to the substrate, respectively. Furthermore, they found that the mutual relationship between n_z and n_{xy} was inversed with T_d lower than $0.8T_{g0}$. These results indicate that the anisotropic structure of the glass samples critically depends on T_d . As to the birefringence of TNB,¹⁰² they reported that a USG sample deposited at $0.85T_{g0}$ initially exhibited anisotropy of $n_z > n_{xy}$, but the difference was diminished as the temperature was raised approaching T_g , and the sample turned to isotropic SCL above T_g .

The one and two dimensional WAXS measurements of IMC glasses⁹³ indicated that the vapor-deposited glasses exhibited an additional broad peak in the small diffraction angle region as well as the broad peak observed for ordinary liquid-quenched glasses. This small angle peak exhibited anisotropy and implied that there was some additional periodicity in the direction perpendicular to the substrate. Similar additional small-angle peaks were also

observed for vapor-deposited glasses of four isomers of TNB⁹⁴ and of nifedipine.¹³⁷ In spite of these studies, the information on the molecular orientation in the glasses has not yet obtained. Ediger et al.⁹⁴ considered that the periodicity of the glass structure in the direction perpendicular to the substrate do not have a relation to the kinetic stability of USG, since there was no correlation between the intensity of the small-angle peak and the relaxation time from glass to SCL.

Yamamuro and coworkers⁷³ studied neutron diffraction from vapor-deposited amorphous CS₂. They found that a broad diffraction peak observed for the room temperature liquid¹³⁸ split into two distinct peaks in the amorphous state at 10 K. This suggested that there appeared new periodicities in the molecular distribution different from that existed in the liquid state at room temperature.

By the MD simulation using trehalose as the model compound,¹¹⁶ it was indicated that stable and dense glasses constructed assuming a vapor-deposited glass had multilayer structures perpendicular to the substrate. This result seems to correspond to the WAXS observations on IMC, TNB, and nifedipine, but it is not clear whether the observed feature is characteristic to USG. The MD simulations on the systems with two-component Lennard-Jones particles^{117,118} gave stable but isotropic glasses.

4.7 Additional remarks on the stable and/or dense glasses

According to the description made in sections 4.2 and 4.3, the USGs studied so far are considered to be dense glasses. However, the possibility of the dense-glass formation depends on compound. To examine the property for the formation of dense glasses, we plotted in Fig. 8 the value T_i of several compounds defined in section 4.3 against the steepness index m .¹⁰⁴ This figure indicates a weak correlation that T_i is smaller for compound with larger m . In other words, the temperature range for the formation of dense glasses is wide for a compound with a larger fragility. The reason of this correlation is not clear at the moment, but Angell pointed out¹³⁹ that this correlation may be related to the Matyushow theory^{140,141} in which the relation between fragility and the distribution of the density of state of the glass was suggested.

There are two standpoints to consider the formation of stable and/or dense glasses by vapor deposition. One is to consider that structures, which are the same as those of

equilibrium SCL states at T_d , are formed by the vapor deposition. Some of the experimental data seem to support this consideration. That is, the densities of the as-deposited samples of IMC⁶² and TNB²⁶ glasses increased as T_d was lowered down to $0.91T_{g0}$ or to $0.85T_{g0}$ along the density curves of SCL, and departed from the curves with the further decrease of T_d . Similar inclination was observed for the T_d -dependence of H of EB glasses,⁷⁴ and also for the behavior of the two-component systems of Lennard-Jones particles^{117,118} studied by the MD simulations.

The other standpoint to consider the formation of stable and/or dense glasses by vapor deposition is that the structures, which are different from those expected for SCL at the same temperatures, are formed by the vapor deposition. The results obtained by us for the formation of dense glasses of alkylbenzenes,²⁹ especially for IPB (see Fig. 10 explained in the next section), seemed to support this standpoint. It should be also noted that, in the case of TL, V_m of the as-deposited samples exhibited the T_d -dependence along the extended V_m curve of SCL in a certain range of T_d and anomalously dense glasses were formed in a narrow T_d -range around $0.95T_{g0}$ exhibiting significant deviations from the above V_m curve (see Fig. 6). We will touch this issue again in section 6.

5. Non-equilibrium in supercooled liquids obtained by heating vapor-deposited glasses through T_g

According to an elementary concept of liquid, a single-component liquid is considered to have only one phase. This is because we usually assume only one chemical species in the liquid. We consider then that the thermal motion of molecules in the liquid is so fast that the most stable state is attained in a short time. However, the discovery of two liquid phases of phosphorus at high temperatures and high pressures¹⁴²⁻¹⁴⁴ and also the prediction of the existence of two SCL states of water on the basis of the discovery of the low- and high-density phases of amorphous water¹⁴⁵⁻¹⁴⁸ woke our interest to find multiple liquid phases of a single compound. On the other hand, the deviation from the Arrhenius behavior of physical properties of liquids at low temperatures^{2,4} has long drawn the attention of researchers. In addition, a vast number of theoretical studies⁶ have been made to explore the relation between the glass transition and the evolution of physical properties of SCLs with the temperature lowering toward T_g . Among them, the hypothesis that molecular clusters are

formed in SCL and their size increases as the temperature is lowered^{6,149} is relatively acceptable from the viewpoint of structural chemistry. The experimental studies¹⁵⁰⁻¹⁵² to explore the phase transformation from one SCL to another SCL are worth remarking in this context.

In our early studies of vapor-deposited molecular glasses,⁹¹ we noticed that EB samples deposited at $0.68T_{g0}$ lost the transparency in a certain temperature region in its SCL state above T_g , while similarly prepared TL samples did not exhibit such phenomena. Later, we noticed²⁹ that the loss of the transparency was due to the light scattering, and also that EB samples prepared at T_d around $0.9T_{g0}$ did not exhibit such phenomena. Furthermore, we detected for EB samples originally deposited at $0.68T_{g0}$ a heat release of a few kJ/mol accompanying the light scattering.⁸³ In Fig.9, the clear difference in the evolutions of the reflected-light intensity in the SCL region is seen for the two EB samples; one was originally deposited as a low-density glass (LDG) at 78 K and the other was a high-density glass (HDG) deposited at 107.7 K.⁸³ Interestingly, vapor-deposited samples of PB and IPB exhibited similar behaviors depending on T_d . In short, PB, and IPB samples originally vapor-deposited as LDG at a sufficiently low T_d tend to exhibit the above light scattering²⁹ and heat release¹⁵³ phenomena, while the samples of these compounds originally deposited as HDG at a T_d close to T_g do not exhibit them.²⁹

We thus consider that the above light scattering accompanied with the heat release was due to the structural relaxation in SCL; that is, the SCL state appearing just after the glass transition from LDG was not in equilibrium and relaxed toward the equilibrium SCL. In this relaxation process, we consider that an inhomogeneity in the density and refractive index appeared and caused the light scattering. It should be noted that the observation of such non-equilibrium phenomena naturally depends on the time scale of the experiment. In our typical experiments, the rate of the temperature elevation was kept to be about 0.3 K/min. Therefore, the non-equilibrium discussed here in relation to the liquid-liquid relaxation was of the time scale of the order of one hour in the low-temperature region slightly above T_g of each compound.

As another example of non-equilibrium in SCL states, we found an interesting behavior of IPB samples originally prepared as HDG. We could sometimes follow the evolution of the light interference in the film samples of IPB and estimated the volume change in the SCL states. Figure 10 displays such evolutions of V_m of the vapor-deposited IPB samples due to the

temperature elevation in the SCL states as well as in glass states.¹⁰³ The horizontal axis represents the temperature and the vertical axis represents the sample volume. The volume is normalized as in Figs. 6 and 7 with V_m of SCL of IPB at T_{g0} . The longest dashed line indicates the extension of the temperature dependence of V_m in the liquid state. Other short dashed lines are the guides for the eyes to indicate the thermal expansion of the non-equilibrium SCLs. We consider these non-equilibrium SCLs had lower or higher densities compared with the equilibrium SCL of IPB. We therefore indicate the above short dashed lines with the abbreviations LDL (low-density liquid) and HDL (high-density liquid).

The LDG deposited at 78.1 K exhibited first a slight thermal expansion up to around 115 K, and underwent a structural relaxation accompanied with volume shrinkage. It exhibited glass transition at 129 K, and underwent another state change in the SCL state at around 140 K being accompanied with strong light scattering. We thus could not determine the scale of the volume for this sample with our light-interference method.

In contrast, the HDG samples deposited at 121.0 and 124.7 K first exhibited small thermal expansions, and underwent rapid structural relaxations accompanied with volume expansions more or less, and exhibited glass transitions. With the further elevation of temperature, these samples exhibited volume increase up to about 154 K, where they started rapid crystallization. We thus estimated the numerical value of their volume in the SCL and glass states by tracing back the fringes of light interference recorded for each sample. We assumed in this process that the V_m of the SCL state just before the crystallization took the value expected by the extrapolation of the V_m curve of the normal liquid of IPB.⁶⁰ Then, we indicate the numerical values of the normalized V_m for these samples as displayed for the lower half of the vertical axis of Fig. 10.

The above V_m evolutions observed for HDL states of IPB samples, which were originally prepared as HDG with T_d close to T_g , clearly indicate that the SCL states just after the glass transition had structures different from those of the SCL states simply expected on the basis of thermal-shrinkage of the normal liquid at higher temperatures. In other words, the SCLs of IPB obtained from HDG through the glass transition were also in a non-equilibrium state just above T_g .

Similar non-equilibrium phenomena in SCL states were reported by Rodriguez et al.¹⁵⁴ for TL samples originally vapor-deposited as stable glasses. They studied C_p of these samples by quasi-adiabatic nanocalorimetry. The samples, which were first deposited at $0.80T_{g0}$, were

annealed prior to the measurements at a temperature higher than T_{g0} and cooled again to the glass state. Then, they performed the calorimetry by raising the temperature, and the resultant C_p curves indicated two peaks of which the relative heights depended on the duration of the annealing. The peak at the higher temperature diminished with a longer annealing time. Rodriguez et al. attributed this peak to the low-enthalpy portion in the original glass which was considered to remain in the sample even after the annealing at a temperature above T_{g0} .

In relation to the behaviors of SCLs obtained from the vapor-deposited glasses, the structures of the crystals appearing from these SCLs are also worth noting. As it is seen in Fig. 9, the SCL states of EB crystallize at around 130 K. We measured X-ray diffraction of such samples,⁹⁵ and found that many Bragg peaks appeared in this temperature region. Unfortunately, the crystal structure of EB is not known to date. However, interestingly, every EB sample appearing from the SCL state exhibited a change in the diffraction pattern at about 145 K. Similar behaviors are frequently seen also for other vapor-deposited alkylbenzenes. Therefore, the structures of the crystals of alkylbenzenes appearing from the deeply supercooled liquid states could be different from those of ordinary crystals obtained by freezing the room-temperature liquids.

6. Our new results obtained for alkylbenzene glasses

In this section, we supplement the contents of section 4 with our new research data.

In section 4.1, the v_d dependence of the stabilities of vapor-deposited molecular glasses was described by referring to the results on IMC and TNB.¹²⁸ Similarly, we have examined V_m of EB glasses by changing v_d . Figure 11 displays the evolution of V_m of EB glasses due to the temperature elevation for the samples deposited at $0.67T_{g0}$ with different v_d . The V_m values of the as-deposited states were smaller as v_d was smaller. In addition, the apparent T_g was slightly higher as v_d was smaller. Let us compare these behaviors with the previously obtained results of the T_d dependence in which v_d was kept almost the same.^{28,29} It is then understood that the condition with slower v_d corresponds to that with higher T_d , and the resultant excess volume of the as-deposited sample becomes smaller.

In our condition of the vapor deposition, the time needed to form one molecular layer on the substrate was 0.1~1 s. It is interesting that this order of time is close to the ordinary criterion of relaxation time at glass transition.^{5,8} It should be also noted that the molecular

diffusion has been reported to be faster at the sample surface than in the bulk of it.^{26,27} Figure 12 displays the plot of V_m against the logarithm of v_d for the as-deposited EB samples which are the same as those indicated in Fig. 11. A similar correlation has been reported previously for IMC and TNB glasses.¹²⁸ Such correlations might be an important clue to clarify the mechanism of the formation of stable and/or dense glasses, although we cannot explain at this moment the mechanism giving these correlations.

In the discussion in section 4.3 on the density of alkylbenzene glasses, we described that these alkylbenzenes form glasses with the densities higher than those expected for the corresponding SCLs at the same temperatures if T_d was chosen appropriately. This statement was based on the approximation mentioned in section 3.5 about the analysis of the light-interference in the film samples. Recently, we obtained results of thermal measurements which strongly support the above description about the density. Figure 13 summarizes the sample-thickness dependence of the heat absorption observed accompanying the thermal expansion due to the structural relaxation preceding the glass transition of dense glasses of TL.¹⁵³ These dense glasses were deposited at $0.82T_{g0}$ and $0.94T_{g0}$ with different initial thicknesses. This figure clearly indicates that the heat absorption accompanying the relaxation was proportional to the thickness suggesting that the relaxation was a bulk phenomenon. Figure 13 also indicates that the molar heat absorption observed for the glasses deposited at $0.94T_{g0}$ was much larger than that for the glasses deposited at $0.82T_{g0}$. This is in harmony with the difference in the apparent amount of volume expansion observed for the glasses prepared at the corresponding T_d s (see Fig. 6). These results strongly indicate that the glasses deposited at $0.94T_{g0}$ had V_m smaller than that expected for SCL at the same temperature.

From the viewpoint of structural chemistry, we are interested in the structures of the thermally stable and/or dense glasses. We are thus making WAXS measurements on these glasses. Figure 14 indicates the summary of the evolution of the peak position of the broad diffraction patterns observed for TL glasses deposited at $0.67T_{g0} = 78$ K and $0.85T_{g0} = 100$ K, respectively.¹⁵⁵ The insertion in Fig. 14 indicates the initial diffraction pattern of the sample deposited at 100 K. This pattern was very similar to those of TL glasses reported in the earlier literature.^{85,86} We infer that the sample in the insertion was initially in the dense glass state, although a sample deposited at a similar T_d was sometimes had the initial V_m almost the same as SCL (see the orange plots in Fig. 6). What is remarkable here is that the peak position of the broad pattern of the dense TL glass (low-temperature region of the red plots in Fig. 14)

was clearly smaller than that of a less dense TL glass deposited at 78 K (low-temperature region of the blue plots in Fig. 14). The blue plots exhibit an increase in the peak position in the range around 105~112 K accompanying the structural relaxation preceding the glass transition, while the red plots exhibit a sudden increase at around 120 K where this sample underwent the glass transition. It should be noted also that the peak positions of the broad diffraction patterns of these two samples showed a good agreement with those in their SCL states after the glass transitions. We can thus conclude that neither the dense ($T_d = 100$ K) nor the less-dense ($T_d = 78$ K) glasses of TL had the structures the same as the simple extension of the structure of the SCL state (dashed line in Fig. 14).

To explore the structures of the thermally stable and/or dense glasses, we are also making quantum-chemical calculations. Although we can examine with recent package software the energy of a cluster of small molecules with a particular intermolecular conformation, it is rather difficult to get information of the various conformations which might appear in the glass state. Recently, Ohno and Maeda¹⁵⁶⁻¹⁵⁸ invented a method for systematically exploring equilibrium and transient structures of atomic or molecular systems, and named the method GRRM (global reaction route mapping). We are applying this method to explore various conformations of TL dimer.

Figure 15 indicates the examples of the structures of TL dimers.¹⁵⁹ In these calculations, the GRRM program was first used with Gaussian09 software¹²¹ at the MP2/6-31G level to explore the different points of local-energy minima. We found 23 different locally stable conformations. After this, we calculated the energies of the representative conformations with the MP2/6-311++G(d,p) level by making the BSSE correction with the counterpoise method.^{160,161} The numerical data indicated in Fig. 15 are the stabilization energies for three representative conformations obtained as the difference from twice the energy of a single molecule.

The characteristic feature in the conformations A and B in Fig 15 is that the two molecules stabilized through the interaction between the π -electron system on one of the molecules and the C-H bond on the methyl group of the other molecule. The three stable conformations among the 23 local-energy minima contained two interactions of this type. The quantum chemical studies of the structures of TL dimers have been made by many workers,^{22,124-127} and structures similar to these displayed in Fig. 15 have been reported already. However, nobody has described clearly the stable structures in terms of the

interaction between the π -electron system and the C-H bond which is frequently seen in crystals of organic compounds.¹⁶² Since the interaction between TL molecules is dominated by the short-range dispersion interaction and the interaction explained above, we consider that such structural information for the dimers are useful in considering the structure of the stable and/or dense glasses of TL. Note that the shoulder in the X-ray diffraction pattern displayed in the insertion in Fig. 14 indicates the existence of a Fourier component of the electron density with the distance of about 0.36 nm. This might correspond to the distance between the π -electron systems on the most closely interacting two TL molecules.

7. Concluding and additional remarks

It has been found in the last decade that the properties of vapor-deposited molecular glasses much depend on the preparation conditions. This is not the situation observed for the glasses prepared by the conventional liquid-quenching method. Researchers especially paid attention to the fact that several compounds form stable and/or dense glasses with the deposition at T_d close to T_g . Such glasses seem to show thermodynamic and/or kinetic stabilities. Thus the results of these studies are expected to be made use of in manufacturing processes, for instance, of organic electric devices. These results are also suggestive for material processing in such as pharmaceutical industry,^{163,164} although we have not referred in this article to the issues in this field of science. It should also be mentioned here that the properties of molecular glasses naturally depend strongly on the molecular structures as well as on the conditions of the sample preparation. In spite of the fairly large number of the studies of the stable and/or dense molecular glasses, the substantial structures of these glasses have not been clarified yet. Further studies of these glasses are desirable from the viewpoint of structural chemistry.

In this article, we also touched the properties of SCLs obtained by heating the vapor-deposited glasses through T_g . Phenomena attributable to non-equilibrium in the sample state are sometimes observed for particular kinds of compounds. This is a new issue in the research of molecular liquids. Finally, the vapor deposition method is now attracting new attentions even outside of the field of molecular materials. Recently, it was reported that polymer glasses⁶³ and metal glasses¹⁶⁵ with T_g higher than those of the liquid-quenched glasses were obtained by this method, although their enthalpies were rather higher than those of the liquid-quenched glasses.

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Table 1 Symbols of quantities and abbreviations of sample states, methods and so on.

T_{cryst}	crystallization temperature
T_{d}	deposition temperature
T_{f}	fictive temperature (see section 4.2)
T_{g}	glass transition temperature in general or T_{g} observed for each vapor-deposited sample
T_{g0}	glass transition temperature reported for ordinary liquid-quenched glass
$T_{\text{g, on}}$	onset temperature of glass transition
T_{i}	low-temperature limit of the range where formation of dense glasses are expected (see section 4.3)
C_p	heat capacity
V_{m}	molar volume
H	enthalpy
n	refractive index
R_{m}	molar refraction
ν_{d}	rate of deposition
τ	relaxation time
η	viscosity
m	steepness index or fragility index
SCL	supercooled liquid
USG	ultra-stable glass
LDG	low-density glass
HDG	high-density glass
LDL	low-density liquid
HDL	high-density liquid
DSC	differential scanning calorimetry
DTA	differential thermal analysis
GRRM	global reaction route mapping
MD	molecular dynamics
SIMS	secondary ion mass spectrometry
WAXS	wide-angle X-ray scattering
OLED	organic light emitting diode

Table 2 Characteristic temperatures of typical compounds used in the studies of vapor-deposited molecular glasses. See Table 1 for the meaning of each symbol of the temperature. Range of the temperature indicates the range observed for samples with different T_d . Abbreviations are given for the compounds referred to frequently.

Compounds	T_g / K	T_{g0} / K	T_{cryst} / K
toluene (TL)	116.5-121.4 ^{a)}	117 ^{b)}	125-129 ^{a)}
ethylbenzene (EB)	116.2-120.2 ^{a)}	115 ^{b)}	128-129 ^{a)}
propylbenzene (PB)	125.5-130.0 ^{a)}	122 ^{c)}	147-153 ^{a)}
isopropylbenzene (IPB)	129.0-133.0 ^{a)}	126 ^{d)}	152-158 ^{a)}
ethylcyclohexane (ECH)	103.7-106.7 ^{e)}	104.5 ^{f)}	130-136 ^{e)}
butyronitrile (BN)	97 ^{g)} , 99.7-101.5 ^{e)}	97 ^{g)}	118-121 ^{e)}
methanol	103 ^{h)}	103 ⁱ⁾	105 ^{h)}
ethanol	96 ^{j)}	97 ^{k)}	120 ^{j)}
propanol	98-102 ^{j)}	96.2 ^{l)}	141-146 ^{j)}
butanol	108 ^{j)}	111 ^{m)}	134-145 ^{j)}
1-pentene	70 ⁿ⁾	70 ⁿ⁾	
propene	56 ^{o)}		
indomethacin (IMC)	310-322 ^{p)}	314.7 ^{q)}	
α,α,β -tris-naphthylbenzene (TNB)	360 ^{r)}	344.8 ^{q)}	

a) Ref. 29. b) Ref. 166. c) Ref. 167. d) Ref. 168. e) Ref. 104. f) Ref. 169.

g) Refs. 14, 15, 17. h) Ref. 11. i) Ref. 170. j) Ref. 99. k) Ref. 171.

l) Ref. 172. m) Ref. 173. n) Refs. 16, 17. o) Ref. 75. p) The values represent

$T_{g,\text{on}}$, Ref. 27. q) Ref. 48. r) The value represents $T_{g,\text{on}}$, Ref. 102.

Table 3 T_{cryst} of compounds for which the crystallization in vapor-deposited amorphous states were studied. Range of the temperature means that the compound crystallizes gradually or via several distinguishable steps.

Compounds	$T_{\text{cryst}} / \text{K}$	References
<i>n</i> -C ₂₄ H ₅₀	80-300	23
<i>n</i> -C ₃₆ H ₇₄	130-290	18
benzene	60	88
naphthalene	105	22
anthracene	200-300	21
biphenyl	140	19
<i>p</i> -terphenyl	140-210	53
chlorobenzene	109	51, 52
1,2-dichloroethane	110	97
butane	59.5	50
pentane	71.8	50
hexane	88.3	50
CS ₂	70	73

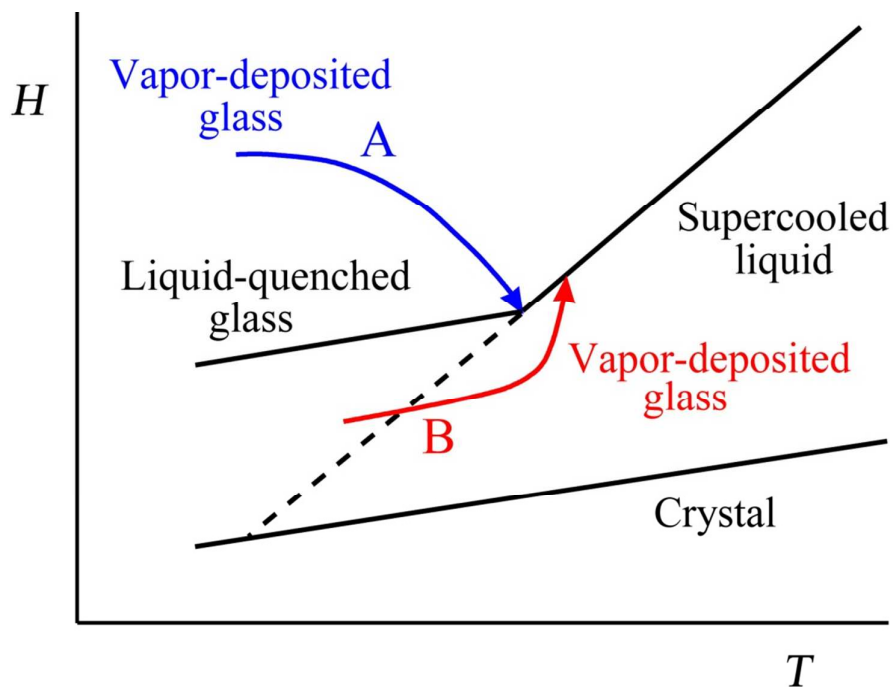


Fig. 1 Schematic presentation of the relations among the temperature dependences of H in different states of a molecular compound. See the text for the symbols A and B. Reproduced from Ref. 25 by permission of the Society of Rheology, Japan.

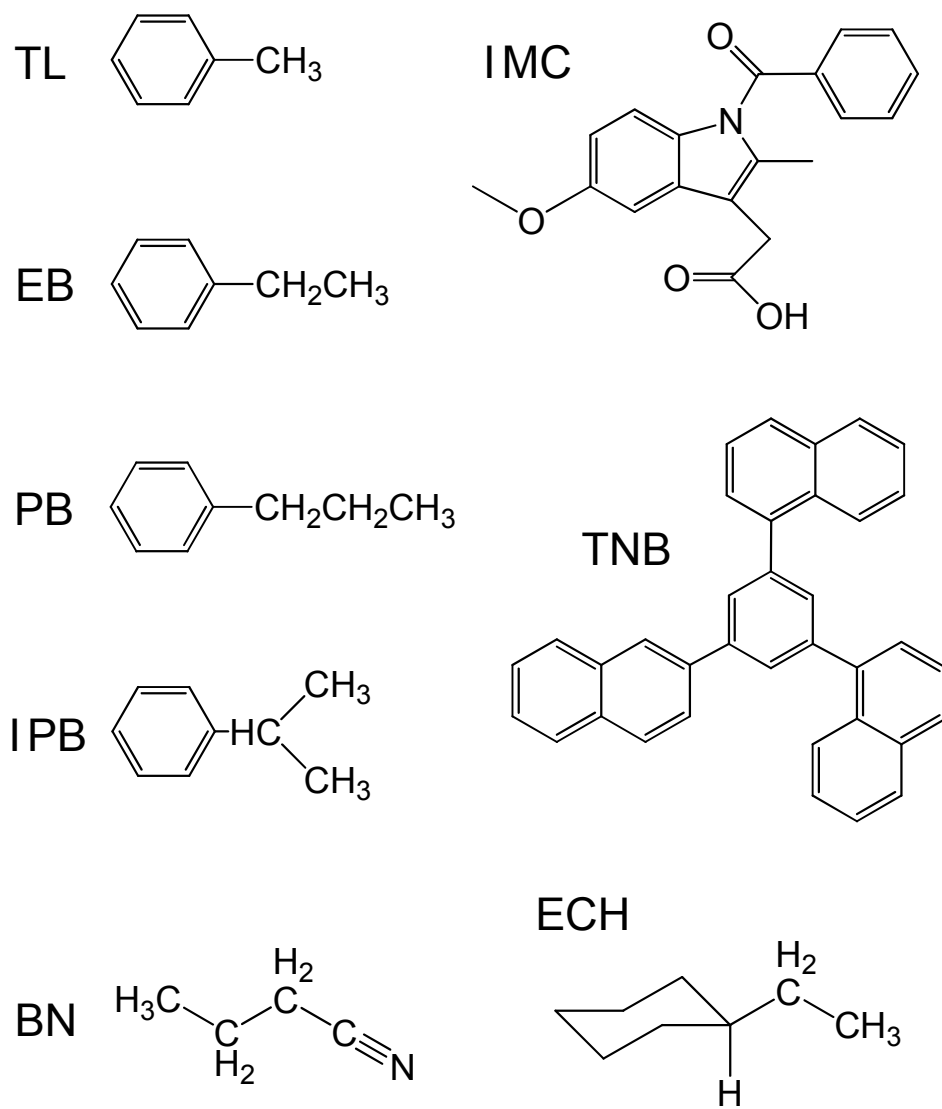


Fig. 2 Molecular structures of typical compounds used in the studies of vapor-deposited molecular glasses.

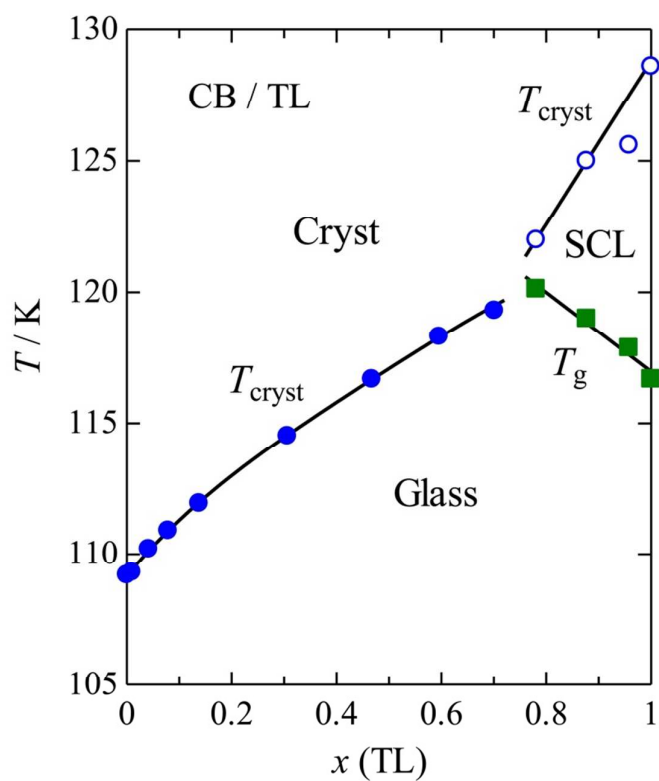


Fig. 3 Characteristic temperature observed in the temperature raising processes of chlorobenzene(CB)/TL binary systems plotted against the mole fraction x of TL. Blue closed circles: T_{cryst} of solid states, green closed squares: T_g of solid states, blue open circles: T_{cryst} of SCL states. Reproduced from Ref. 51 by permission of Springer.

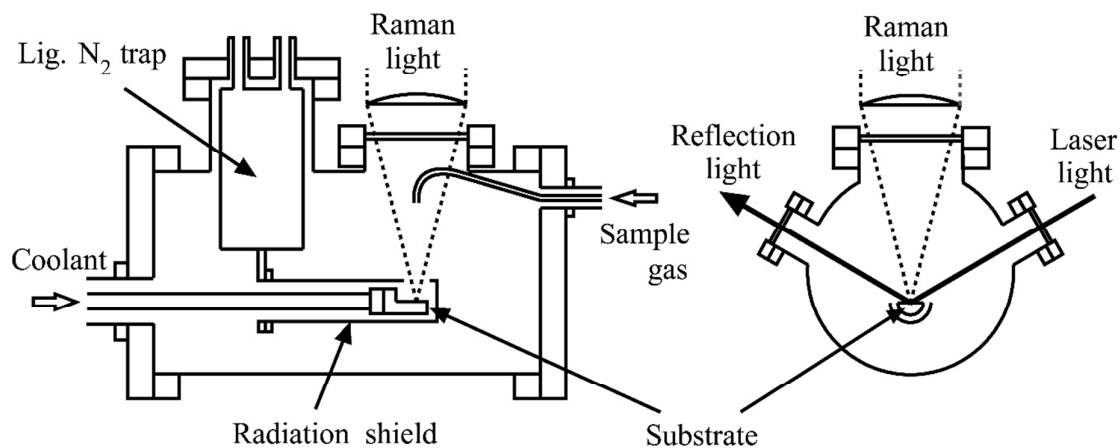


Fig. 4 Construction of a vacuum chamber for the Raman and reflected-light intensity measurements on vapor-deposited glasses. Reproduced from Ref. 24 by permission of American Chemical Society.

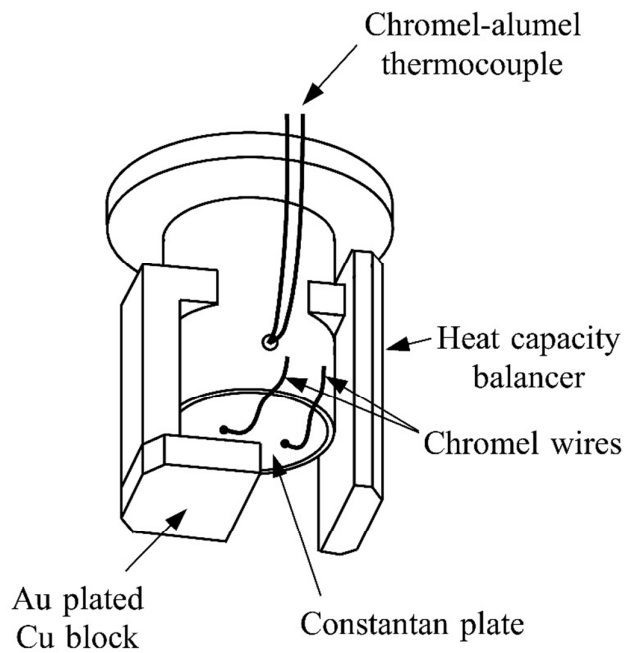


Fig. 5 DTA sensor with a light-reflecting mirror for in situ and simultaneous monitoring of thermal and optical behaviors of a vapor-deposited molecular films.

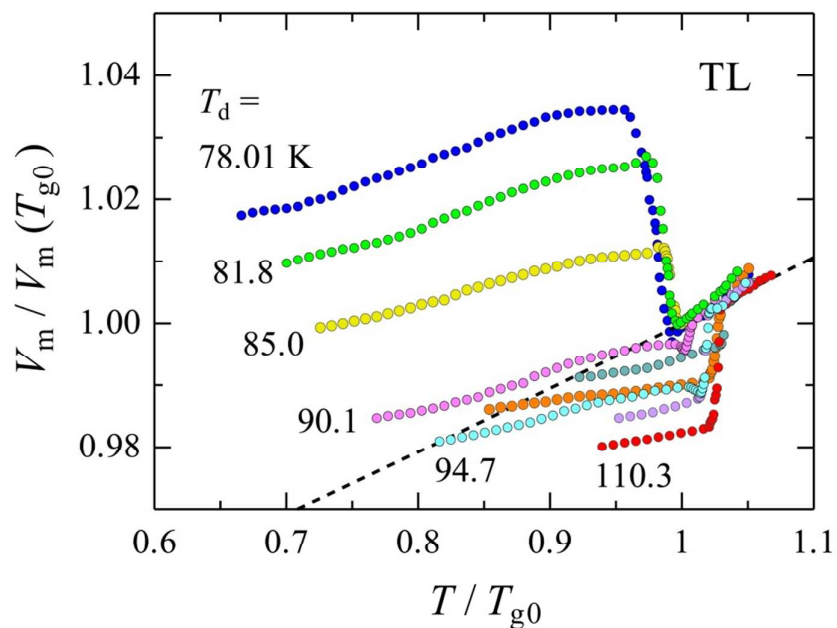


Fig. 6 Evolution of V_m of TL samples deposited at different T_d due to the temperature elevation. Horizontal axis represents the temperature normalized by T_{g0} . Vertical axis represents V_m normalized by the value expected for SCL of TL at T_{g0} . Dashed line represents the extension of the temperature dependence of V_m of TL liquid. Reproduced from Ref. 29 by permission of the Chemical Society of Japan except for the manner of the presentation of axes.

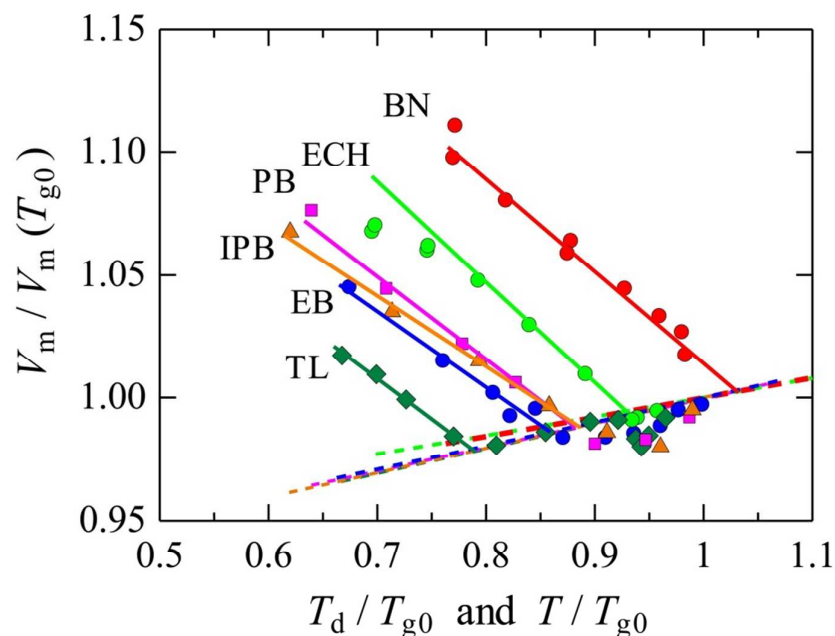


Fig. 7 T_d dependencies of V_m of as-deposited glasses of different compounds. Vertical axis is the same as in Fig. 6. Horizontal axis represents T_d normalized by T_{g0} of each compound and also the temperature of the corresponding SCLs as in Fig. 6. Solid lines are guides for the eye for indicating the T_d -dependence of V_m of the as-deposited glasses. Dashed lines represent the extension of the temperature-dependence of V_m of liquid of each compound. Reproduced from Ref. 104 by permission of American Chemical Society except for the manner of the presentation of axes.

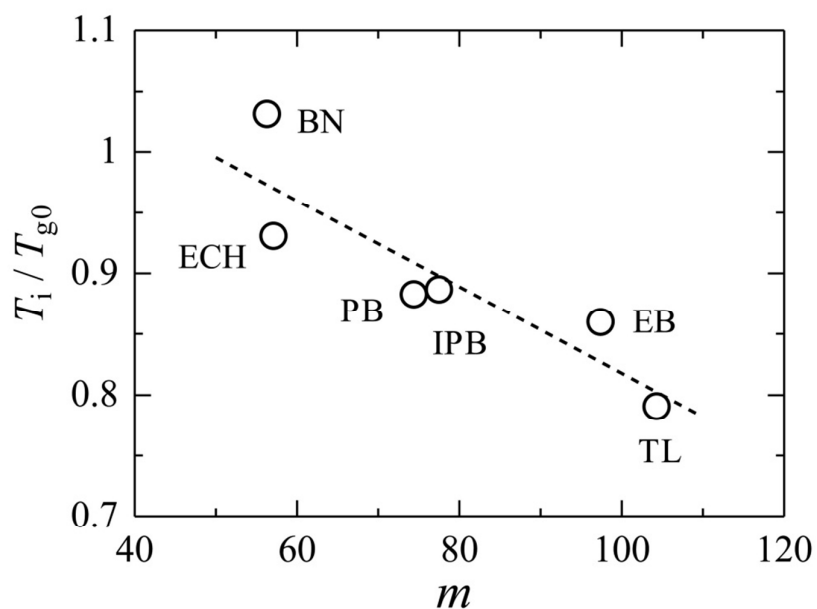


Fig. 8 Correlation between m and T_i of glass-forming compounds studied by us. The vertical axis is normalized in the same manner as in Fig. 6. The dashed line is presented solely as a visual guide. Reproduced from Ref. 104 by permission of American Chemical Society except for the manner of the presentation of vertical axis.

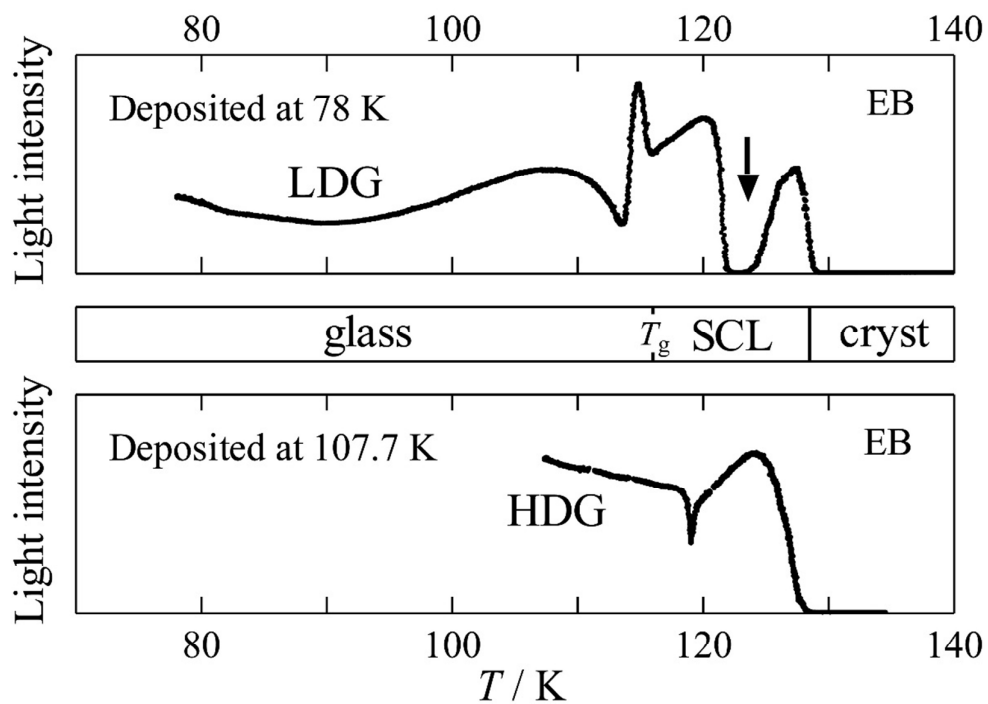


Fig. 9 Comparison of the evolution of the reflected-light intensity of two types of vapor-deposited EB samples, and the temperature regions distinguished with the sample states. Reproduced from Ref. 83 by permission of The Chemical Society of Japan.

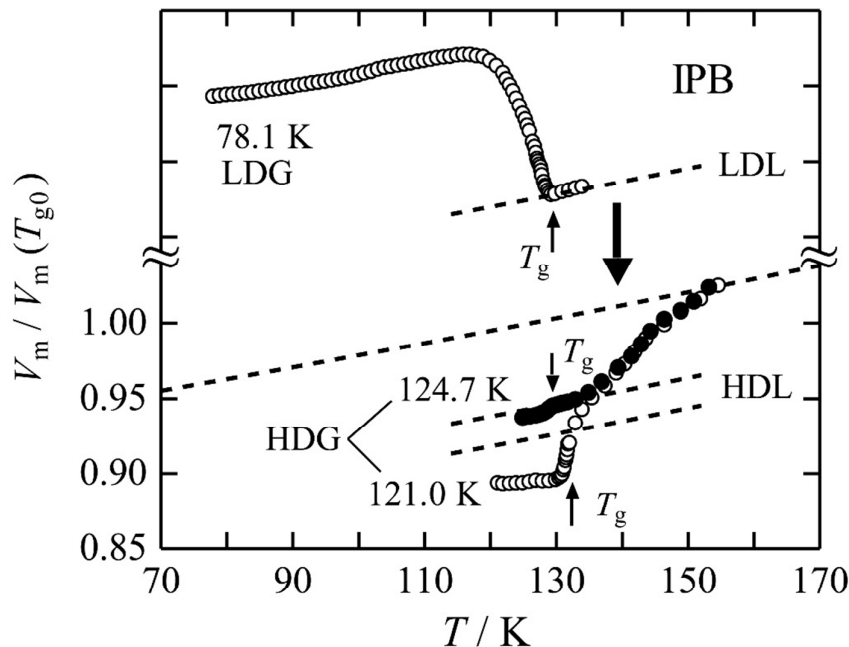


Fig. 10 Evolution of V_m of IPB samples deposited at different T_d . See the text for the explanation of the vertical axis. Closed circles indicate the evolution of V_m of the sample initially deposited as HDG at 124.7 K. Open circles in the bottom part of the figure indicate the evolution of V_m of the sample initially deposited as HDG at 121.0 K. Open circles in the top part of the figure indicate the evolution of V_m of the sample initially deposited as LDG at 78.1 K. Small arrows indicate T_g of each sample. The large arrow indicates the temperature region and the direction of the V_m change at the liquid-liquid relaxation exhibited by the sample initially deposited as LDG. The longest dashed line indicates the extension of the temperature dependence of V_m of IPB liquid. Other short dashed lines represent the levels of V_m of each sample after the glass transition (LDL or HDL), and are guides to the eye qualitatively indicating thermal expansion of each SCL. Reproduced from Ref. 103 by permission of American Chemical Society except for the manner of the presentation of vertical axis.

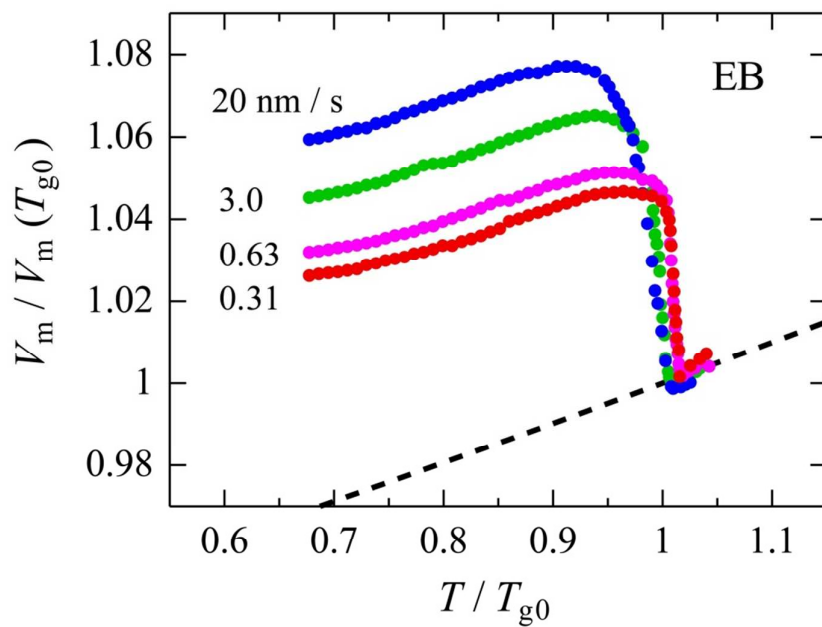


Fig. 11 Evolution of V_m due to the temperature elevation of the EB samples deposited at 78 K with different v_d . The vertical and the horizontal axes represent the V_m and T normalized in the same manner as those in Fig. 6, respectively.

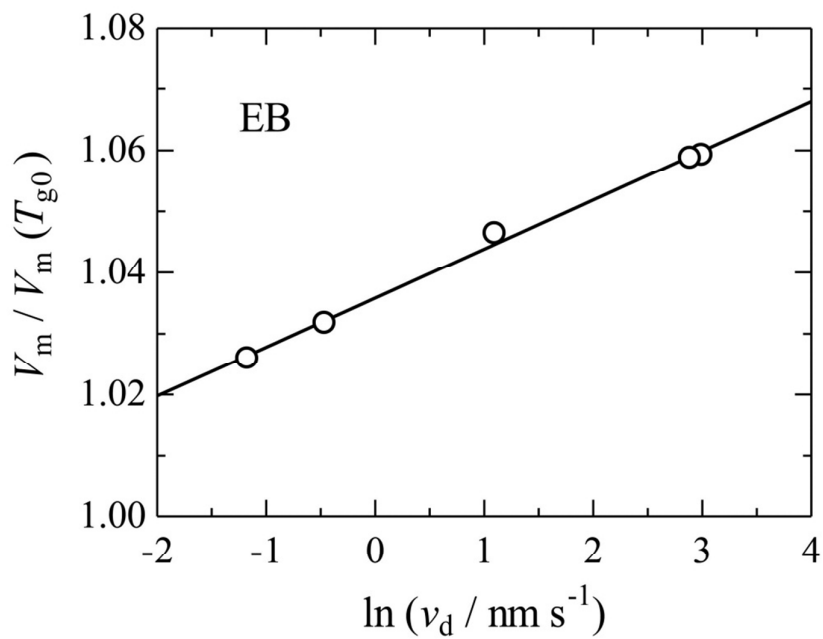


Fig. 12 Plot of V_m against the logarithm of v_d of the as-deposited EB samples which are the same as those indicated in Fig. 11. Vertical axis is the same as that in Fig. 11.

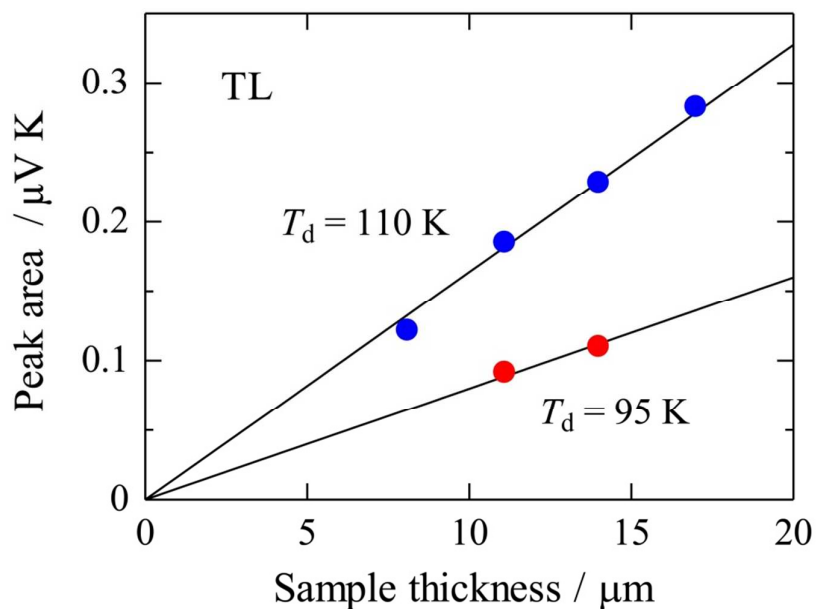


Fig. 13 Sample-thickness dependence of the heat absorption accompanying the thermal expansion due to the structural relaxation preceding the glass transition of dense glasses of TL deposited at 95 K and 110 K. Vertical axis represents the peak area observed in DTA signal.

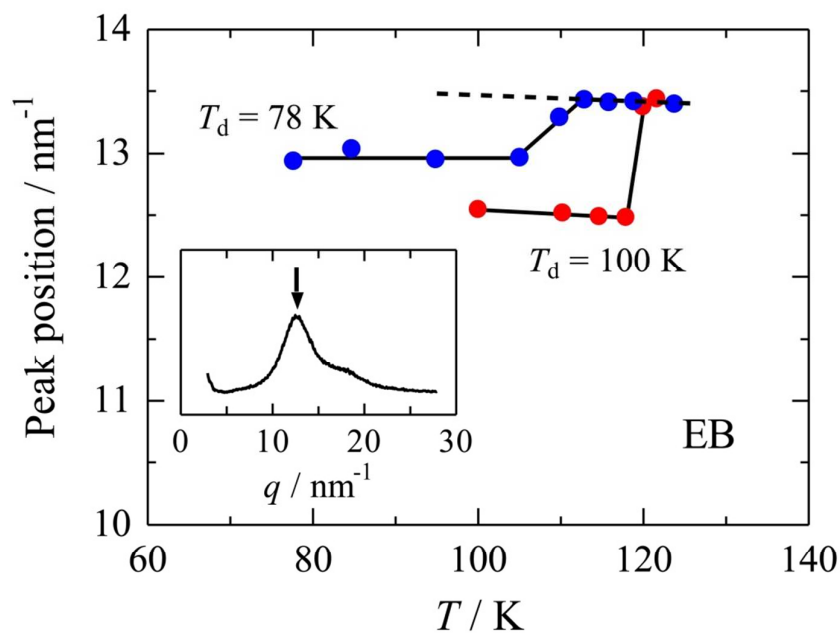


Fig. 14 Evolution of peak position of the broad diffraction pattern observed for TL glasses deposited at 78 K and 100 K with the stepwise temperature elevation. Insertion indicates the initial diffraction pattern of the sample deposited at 100 K. Arrow indicate the peak position.

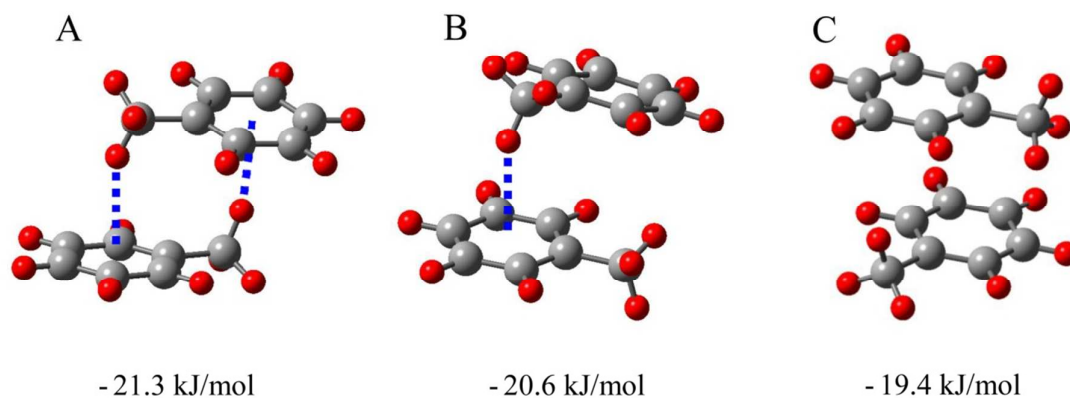


Fig. 15 Examples of the stable conformations and stabilization energies of TL dimers obtained by Gaussian09. The blue dotted lines indicate the interaction between the π -electron system in the phenyl ring and a C-H bond in the methyl group. The exploration of locally stable conformations was performed with the GRRM program, and their energies were calculated later at the MP2/6-311++G(d,p) level by making the BSSE correction with the counterpoise method.